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A COMPARISON OF SEVERAL QUALITATIVE TESTS FOR SOIL ACIDITY

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Although many qualitative tests for soil acidity have been developed during the past few years and satisfactory results have been obtained in some cases, there is still some doubt as to the accuracy of the various methods, when used under certain conditions. Hence it has seemed desirable to study several of the more important methods and to ascertain if possible which tests are best suited for the determination of soil acidity in the field.

For a field test accuracy, simplicity and rapidity are essential. With these factors in mind, a large number of observations were made with various tests on 51 soils secured as follows; 17 from Prof. E. Truog, Wisconsin; 14 from Prof. E. E. DeTurk, Illinois; 6 from Prof. F. L. Duley, Missouri; and the remaining number from various parts of Iowa. The samples were all air-dried, ground to pass a 20-mesh sieve, and tested by the following methods:

1. Hydrogen-ion concentration. Determined electrometrically on a suspension made by shaking 50 gm. of soil and 100 cc. of distilled water in an Erlenmeyer flask for 20 minutes.

2. "Soiltex." Made as recommended by Spurway (9).

3. Truog test. Made as recommended by Truog (10).

4. Comber potassium thiocyanate test. Made by placing 5 gm. of soil and 10 cc. of 95 per cent ethyl alcohol containing 4 per cent of potassium thiocyanate in a 20 by 150-mm. test tube (1). Tube stoppered, shaken 30 seconds and centrifuged 1 minute to secure a clear solution for comparison.

5. Comber potassium salicylate test. Same as the previous test except that a water solution containing 5 per cent of potassium salicylate was used in place of the alcoholic solution of potassium thiocyanate (2).

6. "Richorpoor." A modification of the Comber potassium thiocyanate test, a different solvent being used. Made as in no. 4, with the Richorpoor solution in place of the alcoholic solution of potassium thiocyanate.

7. "The Iowa Test." Developed by Emerson (4), also a modification of the Comber potassium thiocyanate test, a different solvent being used. Distinctive in that it includes a saturated solution of neutral ammonium molybdate in ether which is used when moist soils are being tested.

The LaMotte indicator field set, as recommended by Wherry (11) was tried in connection with this study, but with most soils too much time was required to secure a clear soil extract. This was considered very objectionable since rapidity is one of the essentials of a field test; consequently the results were not included.

TABLE 1

Comparison of qualitative tests for soil acidity made on dry soils and hydrogen ion concentration of soil suspensions expressed in terms of pH values

NUMBER	SOIL TYPE	SOURCE	pH VALUE	SOILTEX	TRUOG TEST	COMBER POTASSIUM THIOCYANATE	COMBER POTASSIUM SALICYLATE	RICHORFOOR	IOWA TEST
1	Gray silt loam	Odin, Ill.	4.60	st.*	st.	st.	st.	st.	st.
2	Yellow gray silt loam	Raleigh, Ill.	4.80	st.	v.st	st.	st.	v.st.	st.
3	Marion silt loam	Unionville, Iowa	4.90	st.	v.st.	v.st.	v.st.	v.st.	v.st.
4	Brown silt loam (loess)	Illinois	4.90	st.	st.	med.	st.	st.	st.
5	Raw peat	Manistique, Mich.	4.90	c.n.b.r.	v.st.	v.v.st.	v.st.	v.st.	v.st.
6	Waverly silt loam	Boone Co., Mo.	4.95	st.	v.st.	v.st.	v.st.	v.v.st.	v.v.st.
7	Yellow gray silt loam†	Raleigh, Ill.	4.95	st.	v.st.	st.	st.	v.st.	v.st.
8	Grundy silt loam	Mt. Pleasant, Iowa	5.00	st.	st.	st.	st.	st.	st.
9	Marion silt loam	Boone Co., Mo.	5.05	st.	st.	st.	st.	st.	st.
10	Waukesha silt loam	LaCrosse Co, Wis.	5.25	st.	st.	st.	v.st.	st.	med.
11	Decomposed peat	Manito, Ill.	5.25	med.	med.+	n.a.	sl.	sl.	sl.
12	Carrington sand	Vinton, Iowa	5.35	st.	med.+	med.	med.	med.	st.
13	Calamus loam	Calamus, Iowa	5.40	st.	st.	sl.	st.	sl.	med.
14	Brown silt loam	Bloomington, Ill.	5.45	st.	med.+	med.	st.	med.	st.
15	Brown silt loam†	Bloomington, Ill.	5.45	st.	med +	st.	st.	st.	st.
16	Carrington loam	Independence, Iowa	5.50	st.	st.	med.	med.	st.	st.
17	Carrington silt loam	Springivie, Iowa	5.50	st.	st.	st.	v.st.	st.	st.
18	Clyde silt loam	Union Grove, Wis.	5.50	med.	st.	med.	med.	med.	n.a.
19	Dune sand	Oquawka, Ill.	5.55	st.	st.	n.a.	sl.	n.a.	st.
20	Yellow silt loam†	Elizabethtown, Ill.	5.60	st.	med.	med.	med.	med.	med.
21	Waukesha silt loam	Galesville, Wis.	5.60	med.	med.	med.	med.	med.	sl.
22	Buckner coarse sand	Muscatine, Iowa	5.60	st.	st.	med.	med.	sl.	sl.
23	Tama silt loam	State Center, Iowa	5.80	med.	st.	st.	st.	st.	st.

24	Red sandy loam	Georgia	5.90	med.	med.	n.a.	sl.	n.a.	med.
25	Shelby loam	Jamison, Iowa	5.90	med.	med.	sl.	sl.	sl.	med.
26	Miami silt loam	Sun Prairie, Wis.	5.90	med.	med.	med.	sl.	sl.	med.
27	Shelby loam	Udell, Iowa	5.95	st.	st.	med.	st.	n.a.	n.a.
28	Clarksville gravelly loam	Lawrence Co., Mo.	5.95	med.	sl.+	n.a.	sl.	n.a.	sl.
29	Yellow silt loam	Elizabethtown, Ill.	5.95	st.	sl.	sl.	sl.	sl.	sl.
30	Miami silt loam	Burlington, Wis.	5.95	med.	sl.+	sl.	sl.	sl.	n.a.
31	Lintonia sand	Mississippi Co., Mo.	6.00	st.	sl.+	n.a.	n.a.	sl.	n.a.
32	Miami silt loam	Stoughton, Wis.	6.05	med.	sl.+	sl.	med.	sl.	med.
33	Waukesha silt loam	Mazomanie, Wis.	6.00	med.	med.	v.st.	v.st.	v.st.	v.st.
34	Miami fine sandy loam	Racine Co, Wis.	6.05	med.	sl.+	sl.	sl.	sl.	med.
35	Miami silt loam	Franksville, Wis.	6.05	med.	sl.+	sl.	sl.	sl.	med.
36	Huntington silt loam	Hickory Co., Mo.	6.15	med.	sl.+	sl.	sl.	n.a.	sl.
37	Marshall silt loam	Missouri Valley, Iowa	6.25	med.	med.	n.a.	sl.	sl.	sl.
38	Baxter gravelly loam	Polk Co., Mo.	6.30	med.	sl.	n.a.	sl.	n.a.	n.a.
39	Carrington silty clay	Union Grove, Wis.	6.50	sl.	sl.+	n.a.	med.	n.a.	sl.
40	Miami fine sandy loam	Racine Co., Wis.	6.55	med.	sl.+	n.a.	med.	n.a.	sl.
41	Gray silt loam†	Odin. Ill	6.65	sl.	sl+	med.	med.	n.a.	med.
42	Carrington silt loam	Caledonia, Wis.	6.70	sl.	sl.+	n.a.	med.	n.a.	sl.
43	Shelby loam	Jamison, Iowa	6.80	sl.	sl.+	sl.	med.	n.a.	med.
44	Waukesha silt loam	LaCrosse Co., Wis.	6.80	sl.	sl.+	n.a.	sl.	n.a.	sl.
45	Miami silt loam	Rochester, Wis.	7.90	neut.	sl.	n.a.	n.a.	n.a.	n.a.
46	Black clay loam	Hartsburg, Ill.	7.95	sl.	sl.	n.a.	n.a.	n.a.	n.a.
47	Decomposed peat	Stoughton, Wis.	8.00	neut.	n.a.	n.a.	n.a.	n.a.	n.a.
48	Webster silty clay loam	Ames, Iowa	8.20	alk.	n.a.	n.a.	n.a.	n.a.	n.a.
49	Black clay loam†	Hartsburg, Ill.	8.55	sl.	sl.	n.a.	n.a.	n.a.	n.a.
50	Clyde silty clay	Burlington, Wis.	8.55	alk.	n.a.	n.a.	n.a.	n.a.	n.a.
51	Knox silt loam	Missouri Valley, Iowa	8.75	alk.	n.a.	n.a.	n.a.	n.a.	n.a.

*st., strong; sl., slight; v., very; n.a., not acid; c.n.b.r., could not be read; med., medium; alk., alkaline; neut., neutral.

†Subsoil.

The method of expressing acidity as recommended by Truog (10) has been followed. In case of "Soiltex" which also differentiates between neutral and basic (alkaline) soils, the nomenclature as given on the Soiltex reaction chart has been used.

The results of the various tests were all made comparable by calling the colors produced by the different tests on soil 1, table 1, strongly acid. All of the other soils were classified according to the amount of color which developed when each of the various tests was used. The data are given in table 1.

A fairly good agreement was secured with all of the tests except in the case of the sandy soils and the acid peats. Soil 5, which is a raw acid peat, would not mix with the Soiltex solution and the acidity could not be determined. Even after the peat had been moistened for several days the test could not be used. Where clear solutions could be obtained, the Soiltex results agreed fairly well with the hydrogen-ion concentration. Very strongly acid soils could not be differentiated from strongly acid soils as indicated by the Soiltex reaction chart. In this test clear solutions are absolutely essential for correct results. Slight turbidity is quite difficult to prevent in clay soils, and in case of heavy dark colored soils, turbidity may darken the color of the solution to such an extent that the soil will appear much less acid than it would if the extract were perfectly clear.

The results secured by the Truog test do not agree quite as well with the hydrogen-ion concentration of the soil suspensions as Soiltex. This is due to the fact that the two tests measure different kinds of acidity. The Soiltex test depends upon the concentration of hydrogen ions in the soil solution which may be considered as the intensity of the acidity. The Truog test measures total acidity, which in some soils may be low but of high intensity; or in other cases, the amount of acidity may be large and the intensity low. For this reason these two methods would not be expected always to give the same results.

The last four methods do not measure soil acidity but measure easily replaceable iron. Comber (1) states, "The color cannot be used as a comparative measure of the lime requirement of different soils; for only iron is identified in this test in a mixture of iron and aluminum which will vary from one soil to another." Carr (3) has attempted to make the method quantitative by titrating the alcoholic potassium thiocyanate extract with standard sodium hydroxide, since both aluminum and ferric hydroxide are completely precipitated when the pH value of the solution is raised above 5.5. This procedure could not be used in the field.

A study of table 1 indicates that the amount of replaceable iron has a relation to soil acidity; and in loams, silt loams and heavier soils, the results secured by tests measuring replaceable iron compare quite favorably with the hydrogen-ion concentration of the soil suspensions. In the case of sandy soils the results were low. In case of soil 33 the results were much too high as compared with the other methods. A further study is being made on this soil.

The Comber potassium salicylate test required much more time than the other tests measuring replaceable iron, because soil colloids settle more slowly in water than in organic solutions. Potassium salicylate cannot be used in other solvents such as acetone which would hasten the rate of settling of the soil because ferric salicylate does not produce nearly as much color in organic solvents as in water.

The Comber potassium thiocyanate and Richorpoor tests gave about the same results. The soils used in this study settled more slowly in these solutions than in the Iowa test solution no. 2, and it was also found that the Iowa test was more sensitive than the Comber and Richorpoor tests giving a light red color in slightly acid soils, a scarlet color in medium acid soils and a dark red color in strongly acid soils.

Comber (1) has noted that the use of an ether-alcohol mixture increased the sensitivity of the potassium thiocyanate test. An acetone solution of potassium thiocyanate dissolves more iron from a soil than the same amount of potassium thiocyanate in either methyl or ethyl alcohol. The addition of ether to the acetone solution of potassium thiocyanate causes a further increase in the amount of iron dissolved. Carr (3) has shown that the acidity of the alcoholic potassium thiocyanate solution was an important factor in the amount of iron extracted from a soil. His results were confirmed in the case of methyl and ethyl alcohol, but it was found that acidity was not important in the case of acetone solutions. When 0.1 cc. of glacial acetic acid and 10 cc. of an alcoholic solution of potassium thiocyanate were added to 5 gm. of a slightly acid soil and shaken, a dark red color was produced. Only a light pink color was secured when the acid was not added. When the same amount of acetic acid was added to 10 cc. of acetone containing 1 per cent of potassium thiocyanate, and shaken with 5 gm. of the same soil, no increase in color was produced over that of a solution of potassium thiocyanate in acetone containing no acid.

EFFECT OF MOISTURE ON ACIDITY TESTS

An accurate field test for soil acidity should give the same results on either moist or dry soils. In the previous experiment only dry soils were used. In this experiment both moist and dry soils were studied under the various methods as given in table 1.

Emerson (4) has recommended the addition of a saturated solution of neutral ammonium molybdate in ether to moist soils before adding the solution containing the potassium thiocyanate. In order to determine how much the different tests were affected by moisture, 12 acid soils and 2 acid peats were selected. Twenty cubic centimeters of distilled water were slowly added to 100 gm. of dry soil. The mass was thoroughly mixed, covered and allowed to stand over night. The water content of the peats was made up in a similar manner to 100 and 200 per cent, respectively. Equivalent amounts of soil

TABLE

Effect of moisture on qualitative tests for soil acidity

NUMBER	SOIL AND SOURCE	H₂O CONTENT	SOILTEX	TRUOG TEST	COMBER POTASSIUM THIOCYANATE	COMBER POTASSIUM SALICYLATE	RICHORPOOR	IOWA TEST*
		per cent						
1	Brown silt loam; Bloomington, Ill.	none	st.†	med.+	sl.	st.	sl.	st.
2	Brown silt loam; Bloomington, Ill.	20	st.	med.+	n.a.	st.	n.a.	v.st.
3	Gray silt loam; Odin, Ill.	none	st.	st.	v.st.	st.	st.	st.
4	Gray silt loam; Odin, Ill.	20	st.	st.	st.	st.	st.	v.st.
5	Yellow gray silt loam; Raleigh, Ill.	none	st.	v.st.	st.	st.	v.st.	st.
6	Yellow gray silt loam; Raleigh, Ill.	20	med.	v.st.	st.	v.st.	v.st.	med.
7	Muck; Manito, Ill.	none	d.t.r.	med.+	n.a.	st.	sl.	st.
8	Muck; Manito, Ill.	100	st.	med.+	n.a.	v.st.	n.a.	st.
9	Clyde silt loam; Union Grove, Wis.	none	st.	st.	med.	st.	med.	v.st.
10	Clyde silt loam; Union Grove, Wis.	20	st.	st.	med.	st.	sl.	v.st.
11	Waukesha silt loam; Mazomanie, Wis.	none	st.	med.	st.	v.st.	v.st.	st.
12	Waukesha silt loam; Mazomanie, Wis.	20	st.	med.	st.	v.st.	sl.	st.
13	Marion silt loam; Boone Co., Mo.	none	st.	st.	med.	st.	med.	st.
14	Marion silt loam; Boone Co., Mo.	20	st.	st.	med.	st.	st.	st.
15	Waverly silt loam; Boone Co., Mo.	none	st.	v.st.	v.st.	v.st.	v.v.st.	v.v.st.
16	Waverly silt loam; Boone Co., Mo.	20	st.	v.st.	v.st.	v.st.	v.v.st.	v.v.st.
17	Carrington silt loam; Springville, Ia.	none	st.	st.	st.	v.st.	st.	st.
18	Carrington silt loam; Springville, Ia.	20	st.	st.	med.	v.st.	st.	v.st.
19	Carrington sand; Vinton, Iowa	none	st.	med.+	med.	sl.	med.	med.
20	Carrington sand; Vinton, Iowa	20	st.	med.+	med.	sl.	med.	med.
21	Tama silt loam; State Center, Iowa	none	st.	med.	st.	st.	st.	st.
22	Tama silt loam; State Center, Iowa	20	st.	st.	st.	st.	st.	v.st.
23	Marion silt loam; Unionville, Iowa	none	st.	v.st.	v.st.	v.st.	v.st.	v.v.st.
24	Marion silt loam; Unionville, Iowa	20	st.	v.st.	v.st.	v.st.	v.st.	v.v.st.
25	Carrington loam; Ames, Iowa	none	st.	st.	st.	st.	st.	st.
26	Carrington loam; Ames, Iowa	20	st.	st.	med.	st.	sl.	st.
27	Raw peat; Manistique, Mich.	none	c.n.b.r.	v.st.	v.v.st.	v.st.	v.v.st.	v.v.st.
28	Raw peat; Manistique, Mich.	200	c.n.b.r.	v.st.	st.	v.st.	st.	v.st.

*Nos. I and II solutions used on moist soil; no. II alone on dry soil.

†st., strong; med., medium; sl., slight; v.st. very strong; v. v.st., extremely strong; n.a., not acid; d.t.r., difficult to read; c.n.b.r., could not be read.

were weighed out in all cases, allowance being made for moisture. One-half as much peat by weight was used. The results are given in table 2.

Soiltex, the Truog test and the Comber potassium salicylate test gave the same results on the moist and dry soils. The Comber potassium thiocyanate test and Richorpoor gave the same results on some samples, but on others lighter colored solutions were secured with the moist soils. The Iowa test gave the opposite results. The moist soil often yielded much darker colored solutions than the dry soil treated with solution II alone. It was also found that when 2 cc. of solution I was added to a dry soil and shaken previous to the addition of the no. II solution, darker colors were secured than when 2 cc. of acetone was added in place of the no. I solution. However, when 2 cc. of

TABLE 3

Effect of drying soils on results secured with Richorpoor and Iowa tests

				RICHORPOOR TEST			IOWA TEST			
							Moist			
NUMBER	SOIL TYPE	H₂O CONTENT MOIST SOIL	pH VALUE	Moist soil	Air-dried at 25° C. for 3 hours	Dried at 85° C. for 3 hours	Solutions I and II	Ether and Solution II	Air-dried 3 hours Solution II	Dried at 85° for 3 hours, Solution II
		per cent								
1	Carrington loam............	26.0	5.2	sl.*	med.	st.	med.	med.	st.	st.
2	Carrington loam............	14.5	5.25	sl.	med.	st.	st.	st.	st.	st.
3	Carrington loam............	16.2	5.30	sl.	med.	st.	st.	st.	st.	st.
4	Carrington loam............	20.0	5.30	sl.	med.	st.	st.	st.	st.	st.
5	Carrington loam............	20.0	5.45	sl.	med.	st.	st.	med.+	st.	st.
6	Carrington sandy loam......	12.6	5.40	neut.	sl.	med.	med.	med.	med.	med.
7	Clinton silt loam	35.0	5.75	n.a.	sl.	med.	n.a.	n.a.	med.	med.

*sl., slight; st., strong; med., medium; n.a., not acid; neut., neutral.

ether containing no ammonium molybdate was added to a soil in place of solution I, equally dark colors were secured which would indicate that the addition of ether to the acetone solution containing potassium thiocyanate, results in a mixture which is capable of dissolving more iron from an acid soil than the acetone solution alone.

A further test was made on 7 field soils containing from 12.6 to 35 per cent of moisture. Each soil was divided into three parts; one portion was left moist, another was air-dried at 250°C. for 3 hours and the third was dried at 85°C. for three hours. The Truog test and the Soiltex gave the same results on all of the samples whether dry or moist. The Iowa test and Richorpoor were then tried. Two cubic centimeters of solution I and 8 cc. of solution II of the Iowa test were compared with 2 cc. of ether and 8 cc. of solution II on the moist soils. Only solution II was used on the dry soils. The results are given in table 3.

*Nos. I and II solutions used on moist soil; no. II alone on dry soil. †st., strong; med., medium; sl., slight; v.st. very strong; v. v.st., extremely strong; n.a., not acid; d.t.r., difficult to read; c.n.b.r., could not be read.

The Richorpoor test gave three different degrees of acidity on the soils used in table 3, depending upon the condition of the soil.   There was practically no difference in the results secured with the Iowa test when solution I was used previous to solution II, or when ether was used before solution II.   These results would indicate that in most cases phosphorus is not an inhibiting factor as suggested by Emerson (4).   When the moisture content of a soil is below 20 per cent, solution II of the Iowa test gives practically the same results on moist soil as with dry soil, if an equivalent amount of soil is tested.   Five grams of dry soil poured into a test tube occupies only about one-half as much space as 6 gm. of soil containing 20 per cent moisture.   For this reason, an error may be made in field tests due to the fact that about the same volume of soil is used for a test whether it is wet or dry.   This difficulty may be easily overcome by adding the test solution first and then the soil until a definite volume of suspension is secured.

It was found also that the fineness of the soil influences the tests measuring replaceable iron.   Acid soils which are pulverized to pass a 60-mesh sieve give a darker color than the same soils ground to pass a 20-mesh sieve.   This is due in part to the greater amount of surface exposed in case of the finely divided soils and also to the short period of agitation.

EFFECT OF VARIOUS ORGANIC SOLVENTS ON COLOR OF FERRIC THIOCYANATE
   AND AMOUNT OF IRON EXTRACTED FROM SOIL WITH VARIOUS SOLUTIONS
   CONTAINING 1 PER. CENT OF POTASSIUM THIOCYANATE.

The color produced by ferric thiocyanate in solution is due, according to Prescott and Johnson (7), to the undissociated molecules.   Natanson (6) found that the addition of ether to an acid solution containing a small amount of ferric thiocyanate caused a marked increase in color which appeared in the ether layer after the solutions were vigorously shaken.   Marriott and Wolf (5) found that the color produced by ferric thiocyanate in an ether solution was not stable enough for quantitative analysis, and suggested the use of acetone which also increased the amount of color by decreasing the dissociation, produced colors which were stable when exposed to light and possessed another advantage of being miscible with water.

In this investigation, when 0.007 mgm. of iron, as ferric chloride, was added to 10 cc. of various organic solvents containing 1 per cent of potassium thiocyanate, it was found that different colors were produced similar to those secured when an acid soil is extracted.   The colors produced by extracting an acid soil with various organic solvents containing 1 per cent of potassium thiocyanate are given in table 4.

When water was added to these various organic solutions, the color began to fade and soon disappeared except in the case of ethyl acetate which is only slightly soluble in water.   It was also found that more iron was dissolved by some of the solutions than others, containing the same amounts of potassium

thiocyanate.   This was tested by shaking 5 gm. of soil and an equal volume of each of the various potassium thiocyanate solutions and centrifuging to secure a clear extract which was evaporated and then taken up with water containing a little hydrochloric acid.   The ethyl acetate solution replaced more iron than any of the others used.   The acetone solution was second in the amount of iron dissolved.   Methyl and ethyl alcohol solutions were about equal, extracting much less iron than the acetone solution.   An aqueous solution of potassium thiocyanate did not extract enough iron to give a color.

A neutral ethyl acetate solution containing 1 per cent of potassium thiocyanate will dissolve some iron from neutral and basic soils.   It is evident that such a solution is not as desirable as an acetone solution of potassium thiocyanate which settles just as rapidly and does not dissolve iron from neutral and

TABLE 4

A study of the colors produced by extracting a soil with different organic solvents containing 1 per cent of potassium thiocyanate

NUMBER	ORGANIC SOLVENT	KCNS	COLOR* COMPARISON	PLATE NUMBER
		per cent		
1	Acetone........	1	Scarlet red †	1
2	Acetone..................................	5	Scarlet red +	1
3	Methyl alcohol..........................	1	Rhodanite pink−	38
4	95 per cent ethyl alcohol..................	1	Light Jasper red	13
5	50 per cent acetone, 50 per cent ethyl alcohol	1	Nopal red	13
6	50 per cent acetone, 50 per cent methyl alcohol	1	Jasper red	13
7	10 per cent acetone, 90 per cent ethyl alcohol..	1	Jasper red−	13
8	10 per cent acetone, 90 per cent methyl alcohol	1	Rhodanite pink	38
9	Richorpoor................................		Nopal red−	13
10	90 per cent neutral ethyl acetate, 10 per cent ethyl alcohol.........................	1	Spectrum red	13

*Color Standards and Nomenclature by Ridgway (8).
†Colors selected with the assistance of A. M. O'Neal.

basic soils.   An acetone solution of potassium thiocyanate also possesses certain advantages over methyl or ethyl alcohol solutions because soil suspensions settle more rapidly in it, more iron is dissolved which gives a deeper color for comparison, and most important of all, it is less affected by moist soils. Also, Emerson[2] has found that potassium thiocyanate was more stable in an acetone solution than in a solution of 95 per cent ethyl alcohol, because of the lower amount of water present in the acetone.   Water decomposes potassium thiocyanate, liberating free sulfur.   The rate of decomposition is not seriously affected by light, but depends upon the amount of water present. For this reason old solutions of Potassium thiocyanate made up in solvents containing considerable amounts of water may give inaccurate results.

[2] Unpublished data.

CONCLUSIONS

Several qualitative tests for soil acidity were studied with 51 soils secured from Wisconsin, Missouri, Illinois and Iowa. All of these tests indicated, in a general way, differences between strongly acid, medium acid and slightly acid soils. Soiltex also distinguished between neutral and basic (alkaline) soils. The fact that this test requires very little equipment is a desirable feature. The chief difficulties encountered were with peat soils and heavy clay soils from which extracts could not always be secured clear enough for comparison with the Soiltex reaction chart.

The Truog test required more equipment than any of the others and also more time to make the test. This disadvantage is probably not so important when the accuracy of the results are considered. The same amount of each material is always measured for the test, which is not the case with the Comber potassium thiocyanate test and its two modifications, Richorpoor and the Iowa test, as they are being used at the present time by county agents and field men. More accurate results would be secured with these tests if calibrated tubes were used into which an accurate amount of liquid is measured and then soil added until a definite volume of suspension is obtained.

The Truog test and the Comber potassium salicylate test were the only methods which gave accurate results on very wet soils. Satisfactory results with Soiltex can be secured on soils which give low results with the potassium thiocyanate test because of the high moisture content. In the case of soils which contained less than 20 per cent of moisture, the Iowa test gave accurate results, while the Richorpoor test did not give satisfactory results except on dry soils.

Different colors are produced when ferric thiocyanate is formed in various organic solvents. These colors are much darker than the color produced when the same amount of a soluble ferric salt is added to an aqueous solution of potassium thiocyanate. This is probably due to the fact that organic solvents decrease the dissociation of the ferric thiocyanate molecules.

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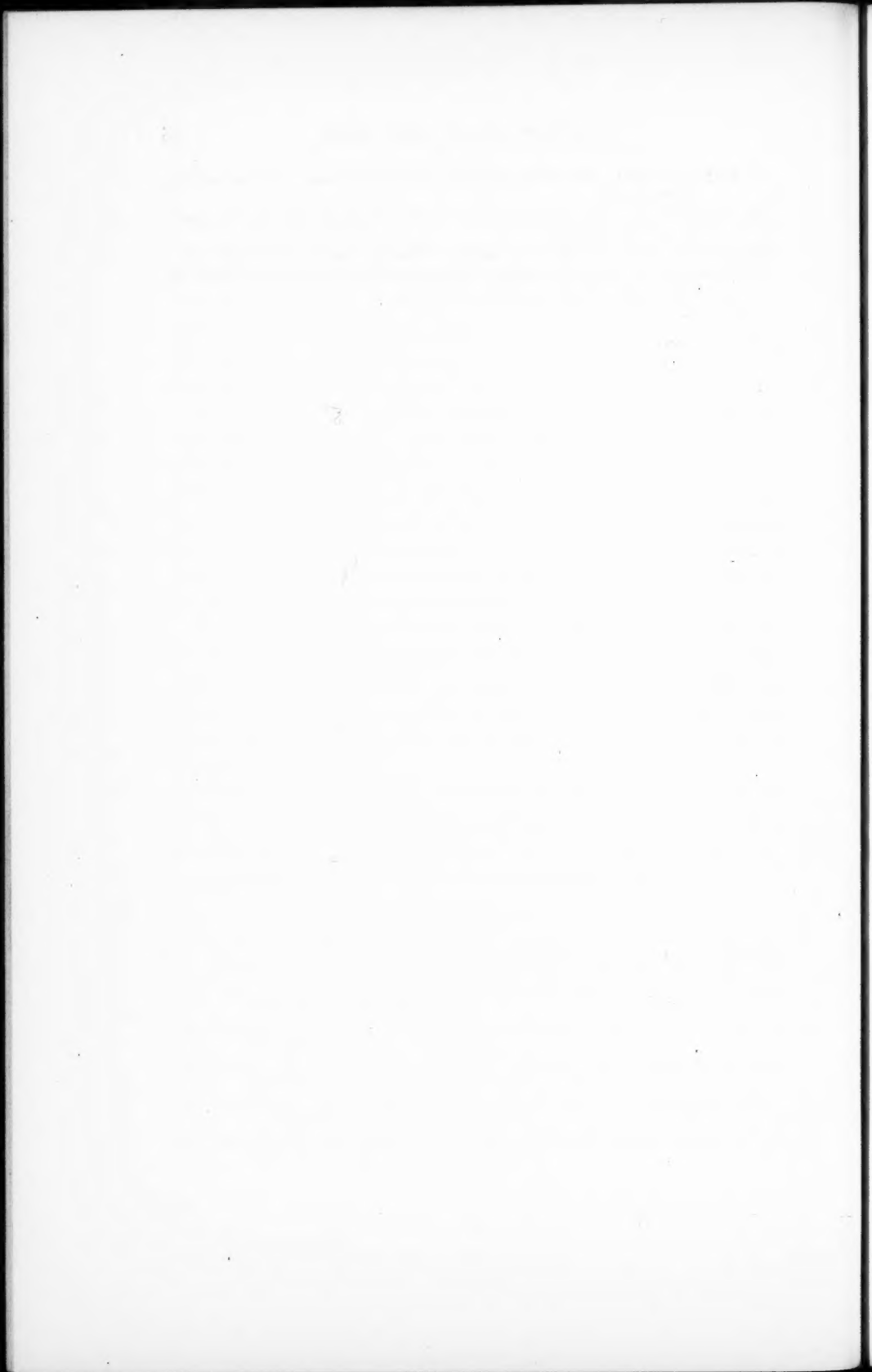
THE COMPARATIVE EFFECTS OF ADDITIONS OF NITROGEN, PHOSPHORUS AND POTASSIUM ON THE NITROGEN ECONOMY OF A WOOSTER SILT LOAM SOIL[1]

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INTRODUCTION

Since nitrogen is one of the most essential plant constituents, is the most expensive to replace in the soil and furthermore is easily lost through leaching, it is obvious that methods of soil management which result in the conservation of the residual nitrogen in the soil and in the most efficient use of the applied nitrogen are of great importance to agriculture.

Such methods of soil management have received a great deal of attention from scientific investigators during the last half century and, although much valuable information has been obtained, nitrogen economy is still a most important problem.

MATERIAL AND OBJECT

The five-year-fertility rotation plots of the Ohio Agricultural Experiment Station are peculiarly adapted to a study of some of the factors which have a bearing on nitrogen economy. These plots on which experimental work was started in 1894 by former Director C. E. Thorne, are among the oldest and most carefully planned field plot tests in this country. The object in starting this work was to study the effects of additions of nitrogen, phosphorus and potassium fertilizers when applied alone and in combination, in different amounts and with different carriers, on the soil and on crop production. It is the object of this paper to discuss the apparent effect of these additions of nitrogen, phosphorus and potassium on the nitrogen economy of the soil.

HISTORICAL

Effect of fertilizer treatments on the conservation of soil nitrogen

It is generally conceded that aside from the removal of nitrogen from the soil in crops, the most serious loss is that occasioned by the leaching out of

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the nitrate nitrogen in the drainage water. Fertilizer applications have a tendency to check this loss. By stimulating crop production they cause a greater proportion of the nitrate nitrogen in the soil to be taken up in the increased crop, thus leaving a smaller amount to be leached out in the drainage water. A part of the nitrogen thus conserved by the larger crop is again returned to the soil in the increased crop residues.

This effect of fertilizer treatment is well demonstrated by the data reported by Russell (7) in comparing two plots, one of which received ammonium salts alone and the other, ammonium salts plus phosphorus and potassium. Although the latter plot produced 67 per cent more grain and over twice as much straw, there was an annual saving by this plot of 16.5 pounds of nitrogen through the more efficient assimilation of the nitrates produced in the soil.

This point is again emphasized in Dyer's (3) discussion of the results obtained in the continuous-culture wheat plots on Broadbalk Field at Rothamsted. Plot 5 in that work has received for 50 years a full supply of minerals without any nitrogen. As compared with the unmanured plot 3, it has yielded annually a crop amounting to 2 bushels of grain and 100 pounds of straw more than plot 3. Notwithstanding this increased removal in crops of about 5 pounds per acre per annum for 50 years, the surface soil of plot 5 contains about 108 pounds of nitrogen more than plot 3 and no diminution is indicated in the second and third depths. Dyer concluded: "This difference is clearly to be attributed to crop residue and the fact that plot 5 is now richer in nitrogen than plot 3 is due to storing up in stubble and root residue of a portion of the natural soil nitrogen, that without mineral manure to aid in its accumulation, would have been lost, as in the case of plot 3, in drainage."

Similar results were reported by Dyer (3) on a series of plots, all of which received the same amount of ammonium salts, but with different amounts of mineral fertilizers. The treatments were made in the years 1852–1893. The results show that as the amount of mineral fertilizer applications was increased, crop production was increased and the nitrogen content of the soil in 1893 was directly proportional to the amount of crop production. Dyer concluded: "The more completely by the supply of minerals the crops have been enabled to utilize the nitrogen supplies, the more have they accumulated in the soil; and conversely, the less that is utilized, the less is retained."

The influence of fertilizer treatment on the nitrogen balance as shown by cylinder and field experiments

The term "nitrogen balance" as used in this paper refers to the difference between the income and outgo of nitrogen in the soil. To determine the nitrogen balance of a soil at least four factors should be known.

 a. The nitrogen content of the soil at the beginning of the experiment.
 b. The amount of nitrogen added in fertilizers, etc.

c. The amount removed in the crops.

d. The amount of nitrogen in the soil at the end of the experiment.

A number of cylinder experiments have been conducted to study the nitrogen economy of different soils. One of the most extensive and carefully planned was reported by Lipman and Blair (4). Their data show the influence of phosphorus and potassium in conserving the nitrogen supply of the soil. A recalculation of their data shows that, in spite of the fact that the crops harvested from the cylinders given this treatment carried away an average of 85 pounds of nitrogen more than the untreated cylinders, the nitrogen balance showed a greater loss of soil nitrogen from the untreated cylinders amounting to 57 pounds. Cylinders receiving lime lost about half as much nitrogen as the unlimed, while those receiving a green manure crop in addition to lime lost about half as much as the limed cylinders.

Taking the average of the cylinders receiving each treatment, the order of the fertilizer treatments with respect to their efficiency in conserving the nitrogen supply of the soil was as follows: (1) P, K, 1N; (2) P, K; (3) Check: (4) P, K, 2N.

Lipman and Blair (5) also carried out a cylinder experiment to test the relative value of nitrogen in the forms of nitrate of soda, green manure crops and stable manure. In this experiment also the addition of the minerals, phosphorus and potassium had a conserving action on the nitrogen supply of the soil, although more nitrogen was removed in the crops on the plot receiving this treatment than on the check plot.

A cylinder test to compare the relative nitrogen economy of four Tennessee soil types was conducted by Mooers (6). He concluded from this test that: "There appears to be throughout the experiments a direct relationship between the size of the crop and the quantity of nitrogen conserved, so that, with other factors constant, the greater the crop, the greater will be the conservation."

A number of field experiments bearing on the subject of nitrogen economy have been conducted. Such an experiment covering a period of 50 years was reported by Dyer (3) in a study of the nitrogen economy of certain variously fertilized plots. The nitrogen balance drawn up for these plots shows that phosphorus and potash have had a considerable influence in conserving both the nitrogen of the soil and that applied in fertilizers.

A recalculation of the data reported by Blair and McLean (2) shows that the order of the fertilizer treatments with respect to nitrogen conservation in their experiment was: (1) P, K, N; (2) P, K; (3) P, N, (4) K, N.

<div align="center">EXPERIMENTAL</div>

<div align="center">*Plan of fertilization*</div>

The general plan of fertilization which has been followed in the five-year-fertility rotation work at the Ohio Agricultural Experiment Station is given in table 1.

During the first five years the quantities of the elements applied to plots 21, 23 and 24 were the same as on plot 11, and the quantities of nitrogen and potassium on plot 30 were slightly smaller.

TABLE 1

Plan of fertilizing of 5-year rotation

Plots 0.1 acre; fertilizing materials in pounds per acre

PLOT NUMBER	ON CORN			ON OATS			ON WHEAT			
	Acid phosphate	Muriate of potash	Nitrate of soda	Acid phosphate	Muriate of potash	Nitrate of soda	Acid phosphate	Muriate of potash	Dried blood	Nitrate of soda
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
1										
2	80			80			160			
3		80			80			100		
4										
5			160			160			50	120
6	80		160	80		160	160		50	120
7										
8	80	80		80	80		160	100		
9		80	160		80	160		100	50	120
10										
11	80	80	160	80	80	160	160	100	50	120
12	80	80	240	80	80	240	160	100	50	200
13										
14	80	80	160				160	100	50	120
15							160	100	50	120
16										
17	160	80	80	160	80	80	160	100	25	60
18	Barnyard manure, 8 tons on corn and 8 tons on wheat									
19										
20	Barnyard manure, 4 tons, on corn and 4 tons on wheat									
21	Same elements as 17, but nitrogen in oilmeal									
22										
23	Same elements as 17, but nitrogen in dried blood									
24	Same elements as 17, but nitrogen in sulfate of ammonia									
25										
26	Same elements as 11, but phosphorus in bonemeal									
27	Same elements as 17, but nitrogen in nitrate of lime									
28										
29	Same elements as 11, but phosphorus in basic slag									
30	Same elements as 17, but nitrogen in tankage									

The block of $30\frac{1}{10}$ acre plots known as section D was selected for the study, since this section received lime on the west half only, and since it has the most uniform topography.

It was not until the beginning of the third complete rotation that lime was applied on section D. Caustic lime was applied at the rate of 1000 pounds per acre on the west halves of all the plots in the fall of 1903 previous to the

corn crop of 1904. In 1909 ground limestone was applied at the rate of 1 ton and in 1914 at the rate of a little over 2½ tons and in 1919 at the rate of about 2 tons per acre.

Data

When the experiment was started in 1894 samples were taken from each plot. Some of these either have been used up in analytical work or were lost, only 17 of them remaining,   These remaining samples were reanalyzed at this time so that the analytical work on both sets of samples might be strictly comparable.   The results of the analyses, together with the number of the plot from which they were taken, are given in table 2.

TABLE 2

Nitrogen content of the soil—1894

PLOT	NITROGEN
	per cent
1	0.1040
3	0.0980
4	0.1000
6	0.1055
7	0.1045
8	0.1120
10	0.0980
11	0.1080
16	0.1115
18	0.1035
20	0.1000
22	0.0940
23	0.1145
24	0.1045
25	0.1130
26	0.1205
28	0.1005
Average............................	0.1055

These samples previously had been analyzed and the data reported (1). Where the results obtained in 1921 differed from those previously reported, they were checked by another chemist.

The methods of sampling and preparation of samples were somewhat uncertain at that early date and since the nitrogen content of the soil as shown by the data varies quite widely from plot to plot, it has been thought advisable in calculating the loss of nitrogen to use the figure representing the average of all the plots.

A set of samples taken from these same plots in 1911 also was available. Some of these had been analyzed and the data reported (1).

As in the case of the 1894 samples, when the results of analysis in 1921 differed from those previously obtained, the determinations were checked by another chemist. The data are given in table 3.

Samples of soil were secured in the fall of 1921. The plots were then in young clover following the wheat crop. A 1-inch sampling tube was used, samples being taken to a depth of 7 inches. Forty borings were made on each

TABLE 3

Nitrogen content of soil 1911 and 1921

PLOT NUMBER	PER CENT OF NITROGEN				NITROGEN—POUNDS PER ACRE			
	Unlimed		Limed		Unlimed		Limed	
	1911	1921	1911	1921	1911	1921	1911	1921
1	0.0905	0.0782	0.0915	0.0813	1,810	1,564	1,830	1,626
2	0.0885	0.0781	0.0920	0.0810	1,770	1,562	1,840	1,620
3	0.0860	0.0746	0.0920	0.0746	1,720	1,492	1,840	1,492
4	0.0855	0.0746	0.0840	0.0746	1,710	1,492	1,680	1,528
5	0.0845	0.0752		0.0781	1,690	1,504		1,562
6		0.0797		0.0831		1,594		1,662
7	0.0810	0.0710	0.0895	0.0776	1,620	1,420	1,790	1,552
8	0.0870	0.0774	0.1030	0.0855	1,740	1,548	2,060	1,710
9		0.0740		0.0801		1,480		1,602
10	0.0640	0.0674	0.0785	0.0712	1,280	1,348	1,570	1,424
11	0.0880	0.0822	0.1010	0.0889	1,760	1,644	2,020	1,778
13	0.0995	0.0822	0.0975	0.0821	1,910	1,644	1,950	1,642
16	0.0915	0.0796	0.0840	0.0766	1,830	1,592	1,680	1,532
17	0.0965	0.0896	0.0980	0.0921	1,930	1,792	1,960	1,842
18	0.1170	0.1040	0.1160	0.1021	2,340	2,080	2,320	2,042
19	0.0930	0.0860	0.0825	0.0835	1,860	1,720	1,650	1,670
20	0.1030	0.0974	0.1010	0.0955	2,060	1,948	2,020	1,910
21	0.0945	0.0891	0.0965	0.0875	1,890	1,782	1,930	1,750
22	0.0890	0.0811	0.0775	0.0723	1,780	1,622	1,550	1,446
24	0.0920	0.0860	0.0970	0.0868	1,840	1,720	1,940	1,736
25	0.0890	0.0816	0.0990	0.0898	1,780	1,632	1,980	1,796
26	0.0855	0.0802	0.0890	0.0786	1,710	1,604	1,780	1,572
27	0.0930	0.0836	0.1000	0.0853	1,860	1,672	2,000	1,706
28	0.0795	0.0764	0.0845	0.0715	1,590	1,528	1,690	1,430
29	0.0885	0.0874	0.0960	0.0844	1,770	1,784	1,920	1,688
30	0.0910	0.0810	0.1050	0.0890	1,820	1,620	2,100	1,780
Average....	0.0897	0.0814	0.0937	0.0828	1,794	1,629	1,873	1,658

of the limed and unlimed plots. The samples were placed in trays as soon as they were brought in from the field, and dried in a chamber designed especially for this purpose. When thoroughly dried, the soil was ground and passed through a 0.5-mm. sieve. The samples were then analyzed for total nitrogen, according to a modification of the Gunning-Hibbard method. The results are given in table 3.

TABLE 4

Nitrogen added in fertilizer 1894–1921

PLOT	POUNDS PER ACRE	PLOT	POUNDS PER ACRE
1	0	17	266
2	0	18	768
3	0	19	0
4	0	20	384
5	456	21	266
6	456	22	0
7	0	23	266
8	0	24	266
9	456	25	0
10	0	26	456
11	456	28	0
13	0	29	456
16	0	30	266

TABLE 5

Total crop production, 1894–1921

PLOT	UNLIMED	LIMED
	pounds per acre	*pounds per acre*
1	46,729	66,328
2	62,589	86,017
3	41,454	65,329
4	36,983	60,350
5	45,981	70,040
6	76,970	96,467
7	38,601	59,807
8	73,425	99,251
9	53,961	79,992
10	39,972	63,624
11	88,343	121,320
13	44,714	69,534
16	41,375	65,713
17	91,641	125,003
18	100,407	128,180
19	47,836	74,834
20	78,711	101,949
21	90,043	112,693
22	42,693	62,421
23	79,709	108,204
24	73,776	113,553
25	47,071	66,494
26	83,209	102,872
28	34,003	55,828
29	83,215	102,703
30	78,091	103,497

Amount of nitrogen added in fertilizer

The amount of nitrogen added to the plots in fertilizer is given in table 4. These figures are not absolute, in that the nitrogen has not been determined by analysis before application in every case. Standard grades of fertilizers have been used, however, and in many cases the claims of the fertilizer companies have been checked by analysis in the laboratory.

Total crop production

The total crop production for each limed and unlimed plot is given in table 5.

DISCUSSION

It at once becomes evident that there has been a marked loss of nitrogen from the soil of these plots. The nitrogen supply of 2110 pounds per acre in 1894 diminished to an average of 1644 pounds in 1921, or a loss of about 22

TABLE 6

Comparative average annual losses of nitrogen and crop production of limed and unlimed plots expressed in pounds per acre

	1894–1911				1911–1921			
	Amount of nitrogen lost from soil		Total crop production		Amount of nitrogen lost from soil		Total crop production	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
Average of all plots...........	17.5	13.1	2,308	2,763	15.0	19.5	1,893	3,388
Average of all checks..........	22.2	21.8	1,589	1,991	14.2	15.9	1,217	2,603
Average of all fertilized plots....	14.4	7.2	2,757	3,245	15.6	22.6	2,315	3,878

per cent. Figures showing the average annual losses of nitrogen and the average total crop production for the periods 1894–1911 and 1911–1921 are given in table 6.

It is interesting to note that in the period from 1911 to 1921, the tendency has been for the loss of nitrogen from the unlimed plots to be lessened, while the loss from the limed ends has apparently been accelerated.

Whether this increased loss of nitrogen from the limed plots is due to the lime stimulating the biological processes, resulting in the breakdown of the organic nitrogen into available nitrogenous compounds which are taken up by and carried away in the larger crops produced on these plots, is not known, since only a few of the crops have been analyzed. The data that are available however, tend to support this view. Also it will be noted that there is a decided increase in the crop production on the limed plots during the period 1911–1921, while on the other hand the tendency has been for the crop production to fall off slightly on the unlimed plots.

Conservation of soil nitrogen through increased yields

The data which bear on the effect of fertilizer treatments as conservers of the soil nitrogen through the more efficient utilization of the available nitrogen are summarized in table 7.

During the progress of the work here reported, a statistical study was made of the data on file, giving analyses of the crops grown on the different plots of the five-year-fertility rotation. The analyses were made on all the crops but for a few years only. After a careful study of these data an attempt was made to calculate the amount of nitrogen removed from each of the plots during the years 1894–1921. While the total amounts arrived at by this method are undoubtedly much too high, there is reason to believe that for comparison of

TABLE 7

Comparison of fertilized plots with regard to crop production and nitrogen conservation

Data expressed in pounds per acre

PLOT	TOTAL CROP PRODUCTION		NITROGEN LOST FROM SOIL		NITROGEN REMOVED IN CROPS (CALCULATED)	
	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
Average check	64,493	41,998	568	556	816	553
2	86,017	62,589	490	548	1,060	788
3	65,329	41,454	618	618	834	543
5	70,040	45,981	548	606	885	600
8	99,251	75,425	400	562	1,252	930
6	96,467	76,970	448	516	1,157	965
9	79,967	53,961	508	630	986	690
11	121,320	88,343	332	466	1,425	1,047
17	125,003	91,641	268	318	1,447	1,086
18	128,180	100,407	68	30	1,550	1,250
20	101,949	78,711	200	162	1,260	998

one plot with another, they come somewhat near the truth. The figures for the most important plots are given with the other data in table 7.

The averages of the total crop production of the limed and unlimed check plots show that the limed plots produced 36 per cent more than the unlimed plots, yet the limed plots lost only 2 per cent more nitrogen from the soil. Chemical analysis of the crops grown on the limed and unlimed ends of these check plots has shown very little difference in the percentage of nitrogen in the crops; the nitrogen content of the crops grown on the limed side is slightly higher, however.

Even if it is assumed that the amount of nitrogen removed in the crops from plots 2, 3 and 5 was the same for each of the plots, the order of nitrogen conservation is identical with the order of crop production, and this is in spite of the fact that plot 5 has received in fertilizer and lost 456 pounds of nitrogen in

addition to the loss of 548 pounds from the store of nitrogen in the soil, making a total loss of 1004 pounds.

Considering the plots which received fertilizer treatments containing two elements, plot 8 which receives phosphorus and potassium gave a greater crop production on the limed end than plots 6 and 9 which receive phosphorus and potassium, respectively, plus nitrogen.

In spite of the fact that they did not produce as large crops as plot 8, plots 6 and 9 lost more of their original supply of organic nitrogen and lost, in addition, the 456 pounds supplied to them in fertilizer.

In the same manner, plot 17, although raising larger crops and receiving only half as much nitrogen, has maintained the nitrogen supply of the soil at a higher level than plot 11.   The application of 8 tons of manure on plot 18 has resulted

TABLE 8

Order of fertilizer treatments with respect to their relative efficiency in conserving nitrogen

ORDER OF TREATMENTS WITH RESPECT TO ABILITY TO CONSERVE THE SOIL NITROGEN		ORDER OF TREATMENTS WITH RESPECT TO ABILITY TO CONSERVE THE NITROGEN ADDED IN FERTILIZER AS WELL AS THE SOIL NITROGEN	
Plot	Fertilizer treatment	Plot	Fertilizer treatment
18	Manure, 8 tons	17	2 P, K, 1 N
20	Manure, 4 tons	8	P, K
17	2 P, K, 1 N	18	Manure, 8 tons
11	P, K, 2 N	2	P
8	P, K	20	Manure, 4 tons
6	P, N	11	1, P, K, 2 N
2	P	6	P, N
9	K, N	3	K
5	N	9	K, N
3	K	5	N

in an increased crop production as compared with 4 tons on plot 20, and has also better maintained the nitrogen supply of the soil.

Another striking comparison brought out in this table is that of the limed and unlimed ends of all the plots.   Disregarding the fact that the calculated removal of nitrogen in the crops of the unlimed plots is only about 80 per cent of that of the limed plots, the data show that with the exception of the manured plots 18 and 20, and plot 3 receiving potash, the unlimed ends of these plots have lost from 50 to 130 pounds of nitrogen per acre more than the limed plots.

The relative efficiency of the different fertilizer treatments in conserving nitrogen is shown in table 8.

In figuring the relative efficiency in conserving both the original supply in the soil and that added in fertilizer, use was made of the calculations of the nitrogen removed in crops.

SUMMARY

1. Cropping a Wooster silt loam soil to a 5-year rotation of corn, oats, wheat, clover and timothy for 30 years has resulted in an average loss of 22 per cent of the original supply of soil nitrogen regardless of fertilizer treatment.

2. The limed ends of the plots have lost, on the average, nearly as much as the unlimed ends.

3. The tendency during the last 10 years has been for the limed plots to lose nitrogen faster than the unlimed plots.

4. Fertilizer treatments have resulted in a conservation of nitrogen directly proportional to the amount of increase in crop production due to the fertilizer treatment.

5. Liming has increased the amount of nitrogen conserved by most fertilizer treatments.

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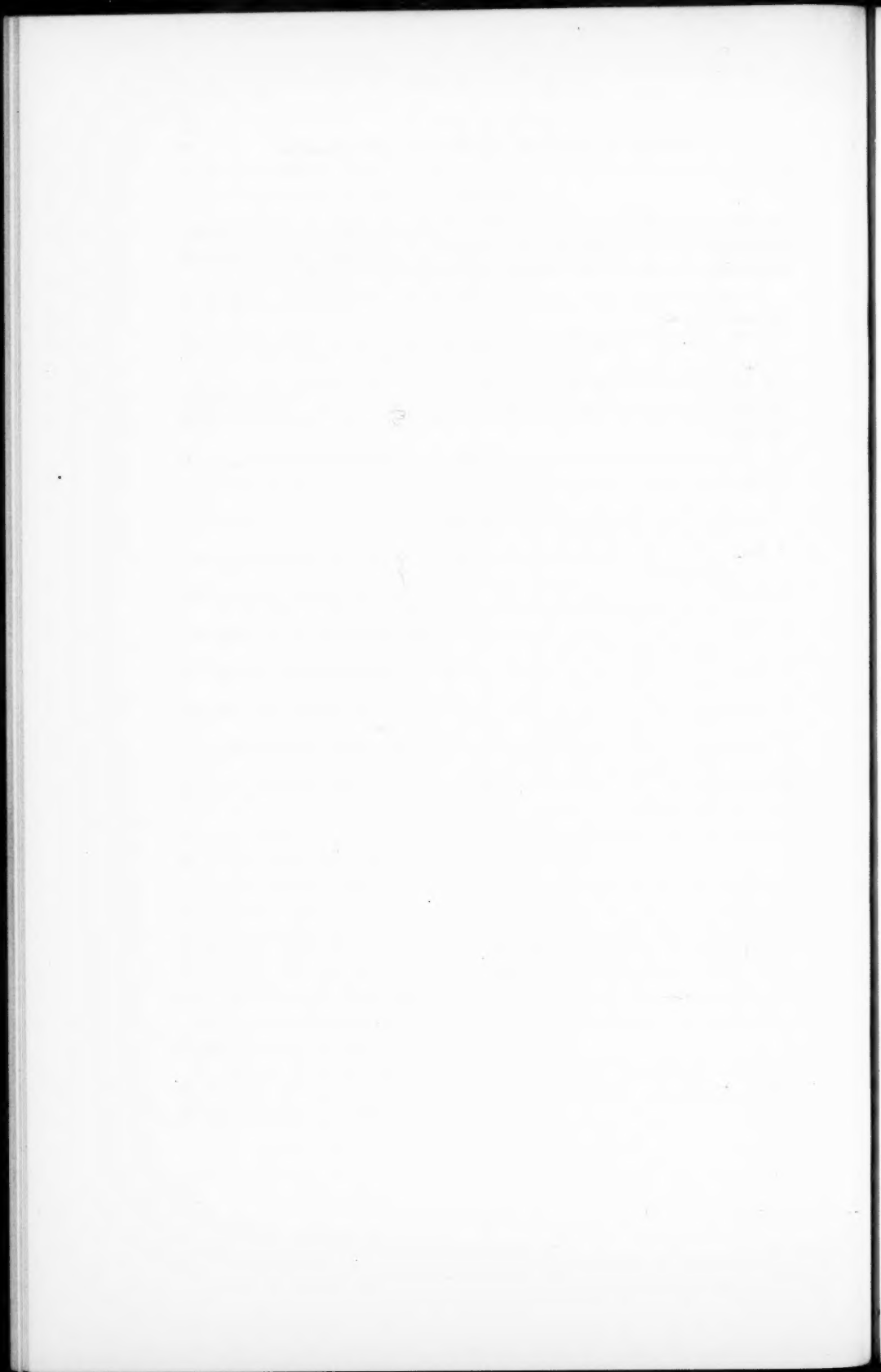
THE INFLUENCE OF THE REMOVAL OF COLLOIDS ON SOME SOIL PROPERTIES

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Michigan Agricultural Experiment Station

In connection with some work at this station, on soil profiles, the effects of the colloidal particles in the soil were strikingly shown by the greater activity of certain horizons when compared to other horizons of similar mechanical composition. Studies have already been conducted upon the isolated colloids, from which it is assumed, one can ascertain the behavior of colloids in soils. But the properties of the colloidal mass when isolated and when disseminated throughout the soil may not be the same, owing to possible changes in the colloids during the process of removal. Since the soil particles of larger dimensions are probably less effected by the technique of colloidal removal than the colloids themselves, it was felt that a comparative study of a normal soil and the same soil without its colloids would be of interest.

To obtain suggestions with respect to this question two acid soils were chosen for a preliminary investigation. One of these soils was a surface sample of sandy loam with a rather high content of organic matter, while the other soil was of similar texture but almost lacking in organic material. Duplicate samples of each soil were suspended in water by shaking in a mechanical shaker for four hours, using a proportion of soil to water of 1 to 3. After washing down the sides of the containers, sedimentation was allowed to proceed for a period of forty-eight hours. At the expiration of this period the supernatant liquid was carefully siphoned off, and one sample of this liquid centrifuged for one hour. This was found sufficient to throw down the silt and clay, leaving the colloidal material in suspension. The solutions were poured off and the silt and clay returned to the mass of orignal soil. The liquid from the duplicate sample from each soil was placed in a Chamberland filter and the liquid passing through was discarded. The suspended material which coated the filter cone was removed and returned to the soil mass. This process was repeated six times. Thus the removal of the greater portion of the colloidal material from one sample and the retention of the same by the duplicate was accomplished, yet each were subjected to the same leaching, washing, and the same amount of shaking. Samples, of the suspended material after centrifuging stood for 15 days without sedimentaton taking place. Thus, while an ultra microscope was not available, it was believed that only colloidal matter had been removed. After drying in the air to a point just below optimum moisture, the samples were screened, mixed thoroughly and stored in air tight containers.

Measurements of (a) the original hydrogen-ion concentration and the amount of lime water necessary to bring about neutralization, (b) the heat of wetting, and (c) the amount of water held free and unfree were made.

HYDROGEN-ION CONCENTRATION

Ten-gram samples of soil were placed in shaker bottles and 50 cc. of neutral distilled water added to one, another received 47.5 cc. of water and 2.5 cc. of 0.04 N calcium hydroxide solution, a third received 45 cc. of water with 5 cc. of calcium hydroxide solution, and so on, to that receiving 37.5 cc. of neutral distilled water and 12.5 cc. of limewater. These were shaken, mechanically, for four hours and allowed to stand twenty-four hours, after which pH readings were made electrometrically. The results are presented graphically in figures 1 and 2.
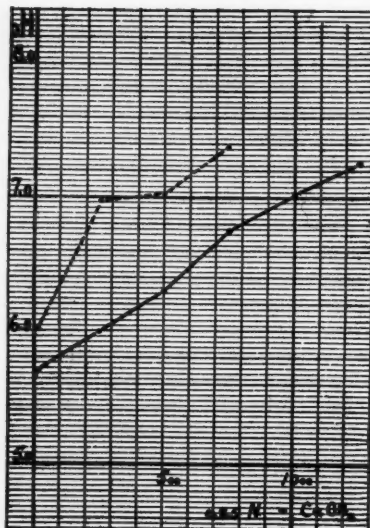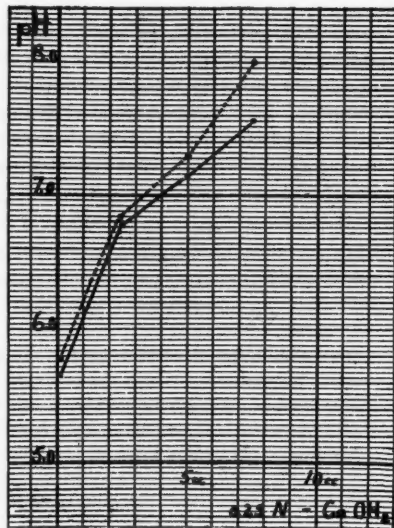
FIG. 1   FIG. 2

——————— Normal Soil
– – – – – Soil minus colloids

FIG. 1. TITRATION CURVES WITH LIMEWATER ON THE SOIL CONTAINING AN ABUNDANT SUPPLY OF ORGANIC MATTER
FIG. 2. TITRATION CURVES WITH LIMEWATER ON THE SOIL ALMOST FREE FROM ORGANIC MATTER

In both soils, the removal of colloids has caused the pH of the original soil to rise, showing less intense acidity in each case. The amount of limewater necessary to bring each soil to the neutral point was less in the case of the soils without colloids. There was less difference in this regard in the case of the sandy loam without organic matter, in which instance, there was but 0.3 cc. difference in the amounts of limewater necessary. The influence of organic colloids seems to be more intense, from the standpoint of buffering and in their

effect of the original pH of the soil.   Bradfield (1) has shown that soil colloids are acid in nature, so that their removal should show somewhat definite changes in pH values and in the response to liming.

HEAT OF WETTING

Samples of about equal weight were measured out and dried in an oven at 105°C. for about thirty-six hours.   After cooling in a desiccator the exact weight of soil was determined, and a thermometer graduated to tenths of one degree inserted into the container in such a way as to cover the bulb with soil. A calorimeter consisting of a thermos bottle of one quart capacity, fitted with a thermometer similar to the one above, and a stirring rod was used.   Into it 100 cc. of pure distilled water was placed, and its temperature accurately read. When the temperature of the soil and water was the same, the soil was quickly emptied into the calorimeter and after stirring to wet the entire mass, the

TABLE 1

Heat evolved by 25 gm. of oven-dry soil on wetting

(Specific heat of soil = 0.2100)

SOIL	AVERAGE OF 2 TRIALS
	calories
Sandy loam with high organic content:	
Normal soil...	103.87
Without colloids..	94.15
Sandy loam with low organic content:	
Normal soil...	32.18
Without colloids..	28.26

temperature was read.   Results have been reduced to the basis of the calories of heat evolved by 25 gm. of oven dry soil and are reported in table 1.

There is a lowering in the quantity of heat set free from soils when the colloidal influence has been removed, but the difference is not as striking as might at first be expected.   The attraction of the surfaces for water is probably the same, whether such surfaces be on a large or a small particle of soil, but the total surface is lowered by the removal of the finer particles.   There may also be a difference in activity of surfaces, in which case the colloidal surfaces would be the most active, and their removal should be factor of importance in the water relationships of soils as shown by these measurements. Further investigation seems necessary in this respect.

WATER RELATIONSHIPS

The dilatometer method in use in this laboratory was employed in this work and freezings made at temperatures of 1.5°C. and 4.0°C. below zero.   According to Bouyoucos (2) the water which freezes at the first temperature is called

free water, while that which does not freeze at this point is called unfree. The latter type of moisture is again divided on the basis of the results from freezing at 4.0° below zero, into capillary adsorbed water and combined water. The capillary adsorbed form fails to freeze at the first temperature, but does solidify at 4.0° below. The remainder, which cannot be frozen at all is the combined form. Duplicate dilatometer determinations were made, which checked closely, and the results reported in table 2 are consequently averages, the total water added being considered as 100 per cent.

In the case of both soils the removal of colloidal material has resulted in a decrease in the amount of combined water held, and a corresponding increase in capillary adsorbed and free forms. It is not clear why the capillary adsorbed form should increase unless the removal of the colloidal coatings of certain larger particles has exposed fresh surfaces and fresh capillaries. In any event,

TABLE 2

Free and unfree water in soil

| SOIL | FREE | UNFREE | |
		Capillary adsorbed	Combined
	per cent	*per cent*	*per cent*
Sandy loam with high organic content:			
Normal soil......	55.98	12.62	31.40
Without colloids.........................	58.02	15.88	26.10
Sandy loam with low organic content:			
Normal soil	60.52	18.78	20.70
Without colloids.........................	62.86	21.18	15.96

these results show the influence of the finer portion of the soil on the combined forms of moisture. These bodies are evidently quite active in causing soil moisture to become inactive. The influence on the available moisture in soils seems worthy of special study.

SUMMARY

The removal of colloids from two soils brought about a rise in the pH value and a decrease in the amount of limewater necessary to bring about neutrality. The heat of wetting was decreased. The amount of water held in the combined form was decreased and the amounts of capillary adsorbed and free water were increased.

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THE INFLUENCE OF WATER ON SOIL GRANULATION

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INTRODUCTION

One of the most interesting physical phenomena in soils is the persistent tendency of soils to assume a granular structure when exposed to certain weather processes such as alternate drying and wetting. Natural soils of the fine-textured type, under normal conditions, nearly always possess this granular structure which is so desirable and important for the ultimate object—the successful growth of plants. In case the granular structure is destroyed by any means the soil soon recovers it upon being exposed to the above weather process. Even when a soil is worked to a plastic condition and becomes as dense and hard as a rock upon drying, it will crumble to a granular condition upon being subjected to alternate wetting and drying.

While there are several other factors or agents which tend to bring about a granular structure in soils—for example, freezing and thawing, addition of organic matter and lime, action of plant roots and animals, and tillage operations—the factor of alternate wetting and drying is probably the most important because it is universal and seems to be the most fundamental and most active.

However, there appears to be much vague and contradictory knowledge concerning the manner in which the process of alternate wetting and drying tends to cause granulation. It is the purpose of this paper, to point out what appears to be the true manner, and to emphasize the important rôle that the water plays in the process.

PREVALENT HYPOTHESIS

The formation of granular structure in soils as influenced by the process of alternate drying and wetting, is quite generally attributed to the pulling or contracting forces of the water films in the soil. It is claimed that as the moisture content of the soil is reduced by evaporation, the pulling power of the thinned water films is increased and they tend to bring or draw together the soil particles into granules, or floccules. This general idea is well expressed by Fippin (2), who says:

In studying these results one is led to inquire as to the force which brings this change or granulation. Clearly it is the water film. As the water content of the soil is reduced the sur-

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face tension comes into play and draws the particles together. The smaller the particles the more easily they will be carried by this film. If the whole film around the wet soil mass contracted uniformly and as a unit the contraction would be manifested chiefly by withdrawal from the walls of the vessel and one dense mass would result. As a matter of fact the puddled soil is not homogeneous. There are inequalities or lines of weakness and these should determine the location of cracks. It also suggests that neither the continued wet condition nor the continued dry condition brings about any change in structure. The contraction of the water film is the primary force and it acts in conjunction with lines of weakness to bring about granulation. Anything which produced a line of weakness in the soil mass would determine the location of a crack.

Along the same subject Cameron (1) says:

The function of the film water in maintaining the soil structure is undoubtedly important . . . . The individual grains of soil are gathered into groups or floccules. While other causes may be more or less operative in particular cases, it seems very probable that the film water is primarily the agency holding together the grains in these floccules. The obvious explanation is that the film is exerting a holding power because of its surface tension. It follows, therefore, that anything which affects the surface tension of water should affect the structure of the soil, that is, the flocculation or granulation of the particles.

In further proof of the prevalence of the film hypothesis may be quoted Searle (3) who says:

The more general idea (which states facts rather than explains them) is that, as the water is removed, any which remains draws the clay particles together into a smaller and denser mass.

Inadequacy of present hypothesis

Upon critical examination, the actual facts not only fail to support the water film hypothesis as accounting for the granule structure in soils, but even contradict it. In the first place, it must be remembered that soil granulation signifies not only the combining of the single particles into compound particles or groups but also the breaking down or crumbling of dense masses of soil such as are found in compacted and puddled soils, subsoils, clods, etc., into loose and granular structure. If the water films tended to draw and hold the soil particles together, it logically follows that the soils would tend to remain in the dense condition and would not be reduced or crumble into the loose and granular structure.

In the second place, experimental evidence goes to show that the existing granular structure of soils under field conditions is due infinitely more to the breaking down or crumbling process than to the combining of single particles by the water films. As a matter of fact the part that water films play in the combining of single particles into compound particles is probably insignificant in comparison with the part that other factors play such as the flocculating agents, cementing materials, cohesive forces, etc.

In the third place, the power of water films to draw particles together or to cause the contraction of large masses of soil, as water is being withdrawn, seems to be greatly exaggerated. Considering the large friction and adhesive-

cohesive forces that the particles will have to overcome in moving at the low moisture content at which films operate, it does not seem reasonable and possible that water films have the pulling power to move and draw particles together.   And some experiments which have been performed seem to support this contention.   For instance, if single particles of clay are suspended in water upon glass, and care is taken to keep them apart during suspension, it is found that they do not come together as the water is reduced to films.

Probably one of the main reasons for attributing large pulling forces to the water films is the contraction of soils as they lose water.   But examination shows that contraction and cracking will begin when the moisture content is still high and is probably not entirely reduced to films.   For instance, some clay soils may have as high as 45 per cent of moisture when the contraction and cracking commences.   Now it seems reasonable to assume that films cannot exert much pulling force until they are considerable reduced in thickness.

These latter facts, therefore, indicate that the contraction of soils is probably due to some force other than the pulling of the water film.

THE TRUE RÔLE OF WATER IN SOIL GRANULATION

From experimental studies that have been conducted as well as from logical reasoning it appears that water plays a leading rôle in the granular structure of soils but in a different way, and indeed just the opposite way, from what is commonly believed and expressed in the foregoing quotations.   Water tends to draw apart or separate the particles from dense formation rather than draw them together.   If the latter were true then there would be no loose and granular tilth of soils, but dense mass or clods.   As has already been stated and as will be seen from plate 1, when clay soils are puddled and allowed to dry they become exceedingly dense and hard, and require tremendous pressure to break or crush them.   If they are remoistened, however, and allowed to dry it is round that they are no longer as dense and hard as before, and require only a small pressure to break or crush them.   If the process of drying and remoistening is repeated a few times, they may even crumble into granules or fine loose-textured pieces.   In some soils, this crumbling may take place with only one wetting.   Examination of the granules or small pieces shows that their single individual particles are held together in a rather loose condition and can be crushed easily by small pressure with the fingers.

This loosening of the particles of crumbling of the solid and dense masses of soil into granules or smaller pieces of loose structure, goes to prove that, on moistening, the water tends to loosen or separate the particles from too close contact and that on drying they do not come back to the original condition.

There appear to be at least two ways in which water is able to bring about a loosening of the solid mass and its final crumbling into granules or smaller pieces.   These are (a) the swelling of the soil colloids and (b) the diminution of the attractive and cohesive forces of the soil particles by the intervening water.

As is generally known, soil colloids, and especially certain types, tend to expand or swell upon absorbing or being wet with water. When the dry dense solid masses of colloidal soils as described above, absorb water, they expand or swell, and their particles are loosened and pushed further apart, sometimes beyond molecular and attractive distances. When these masses of soil dry, the water films are not powerful enough to pull the particles together into as compact or dense condition as they were originally, but allow them to remain in the loose condition into which they were brought by the swelling. Upon further wetting and drying, the soil particles come further apart and they may finally crumble into granules or small pieces.

The loosening, pulling apart and shattering effect of the swelling of the colloids on the particles of the dry dense mass of soils is analogous to that of the freezing of water. The expansion that the water produces upon freezing shatters and pulls apart the soil particles and upon drying, the mass may crumble into granular structure.

The swelling of the colloids tends to facilitate the formation of granular structure in still another way, that is, by the unequal expansion that soil may undergo during the absorption of water. If the soil is moistened unequally, and unequal expansion takes place, there will be stresses set up which will tend to crack or shatter the soil mass.

The second way in which water is able to bring about a loosening of the solid mass and facilitate the development of crumb or granular structure, is by saturating the soil with an excess of water. It can be demonstrated easily that when a solid mass of soil is placed in an excess of water it immediately begins to slake or disintegrate into small floccules as shown in plate 1, figure 3. The process is really a mechanical dissolution somewhat similar to a chemical dissolution, but differing in degree. It is brought about by the attraction of the particles for water, and the film of water intervening or surrounding the particles destroying their force of cohesion or attraction for each other. When the mass is allowed to dry again the particles are no longer as close together as they were before and can easily be crushed. If the particles do not exist in an extremely fine state, and if too much cementing material is not present, after the soil mass is dried it may be left in a crumb structure or in a condition in which it can readily be reduced to crumb structure.

It must be emphasized that water is able to bring about the foregoing physical-structure in soils under conditions in which not much pressure is applied to press and interlock the soil particles together and thus destroy the loosening and crumbling effect of water. From this point of view it would seem that when a clay soil under field conditions has been puddled it would be better to plough it in order that the particles may be free of side pressure and have greater freedom to crumble. But even in unploughed condition, puddled clays tend to assume the granular or crumb structure by the process of wetting and drying.

The question now may be raised to the effect that if it is not the film of water that pulls the soil mass together as water is being withdrawn, what is it? The answer seems to be that it is the pulling forces of cohesion of the soil particles. The soil particles, of course, possess cohesive force, which is developed by the water, the degree of development depending to a great extent upon the colloidal content present. As the excess of water is withdrawn the colloids which had swollen, shrink and the cohesiveness, together with the interlocking of the soil particles, keeps the whole mass intact, and the mass shrinks or contracts as a whole. However, if there is too much friction for the whole mass to contract uniformly, it will crack and separate at the weakest points of contact, or at the most convenient point, or where the greatest pressure is brought to bear. The finer the particles and the closer they are together the greater will be the cohesive force and the denser will be the condition in which the mass will dry. For instance when a plastic clay is moulded into a ball or suspended into an excess of water and then allowed to dry, in either case the dry masss will be as hard as a rock. This hardness is due to the close packing and interlocking of the particles which are thus brought in closer range of molecular attraction and consequently of cohesive force, and also due to the cementing of the colloidal gels and certain inorganic salts. But as previously stated, when these dry and highly dense soils are moistened their particles are pushed apart, their range of molecular attraction and cohesive force is thereby decreased, and consequently the soils do not become as dense and hard when dried again.

No attempt has been made to discuss all the details that are involved in the process of granulation of soils as influenced by drying and wetting. It is purposed simply to show that water tends to granulate soils by its expanding forces rather than by its contracting forces.

SUMMARY

This paper presents a critique upon the rôle of water films on soil granulation. The general idea that the granule formation of soils is due to the pulling forces of the water films as it becomes thinned, appears to be incorrect. If it were correct, then the soil would tend to contract as a mass and into a dense structure condition, and there would be no granular structure. Soil granulation signifies not only the flocking together of the single particles into larger or compound particles, but also the breaking down or crumbling of dense masses of soil such as are found in dry puddled soils and clods, into the loose and crumb structure.

On the contrary, water brings about the formation of granular structure not by pulling the soil particles together but rather by pushing them apart, and thus giving rise to the crumbling of dense masses or clods into the loose and granular structure.

Water is able to accomplish this in two ways: (a) by the swelling of the colloids and (b) by diminishing the cohesive force of the particles as it (the water), comes between them and pushes them farther apart.

The forces of contraction are not due to the water films but to the cohesive force of the soil itself. Water, therefore, plays a very important part in the granulation of soils, but in just the opposite way from what is commonly believed.

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PLATE 1

ILLUSRATIONS SHOWING THE TENDENCY OF WATER TO CAUSE DENSE AND HARD MASSES OF SOIL TO CRUMBLE INTO GRANULAR STRUCTURE

Fig. 1. The ball to the extreme left is as hard as rock; upon being moistened it cracks and begins to crumble as shown in the balls to the right.

Fig. 2. Block to the left is as hard as rock; upon being moistened it cracks and begins to crumble as shown in the next block of soil.

Fig. 3. Ball at the center is as hard as rock; upon being placed in excess of water it slakes into fine granules. When these granules dry, they are in a loose condition.

FIG. 1

FIG. 2

FIG. 3

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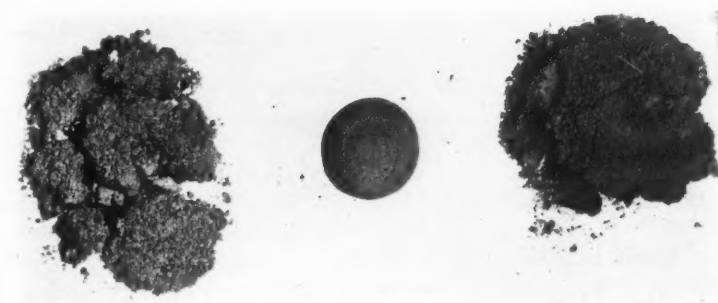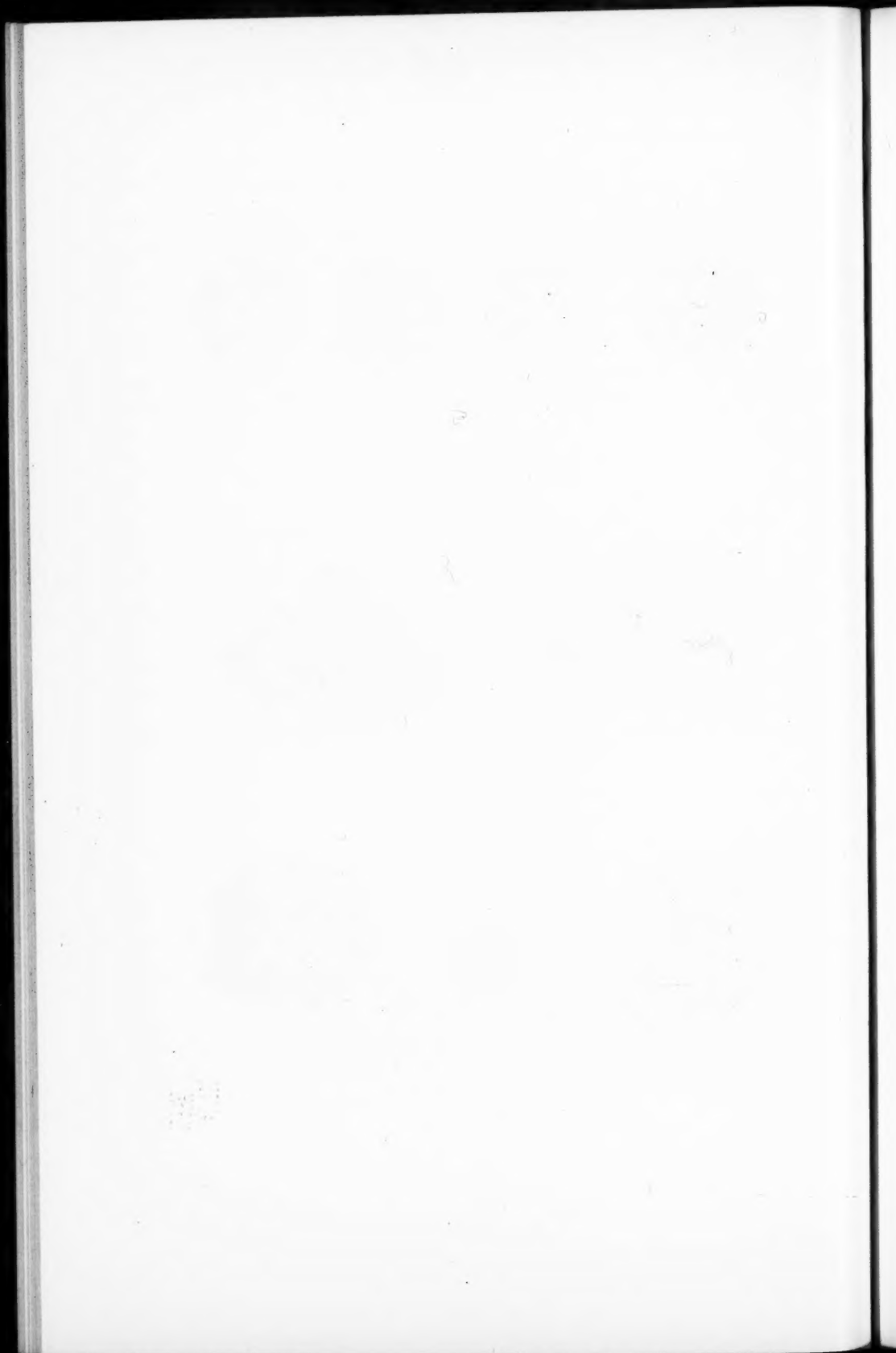
SOME EFFECTS OF SULFUR ON CROPS AND SOILS[1]

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Considerable attention has been given recently to the use of sulfur as a fertilizer and its effect on the soil. In the experiments here reported the author tested the influence of sulfur on the germination and early growth of clover and alfalfa, and its effect on the acidity and solubility of the soils used. Also, the effect of leaching on the acidity produced by the sulfur treatment was investigated.

The experiments were conducted on a Coloma medium sand and a Miami silt loam. The sulfur to be used was washed with distilled water until it gave no freezing-point depression, and then was mixed with the Coloma sand at the rates of 0, 500, 1000, 1500, 2000, and 3000 pounds per acre, and with the Miami silt loam at the rates of 0, 1500, 2000 and 3000 pounds per acre. The former soil was made up to 10 per cent water content and the silt loam to 16 per cent. They were then stored in the dark, the moisture content being kept uniform during the course of the experiment by frequent weighing and the addition of water. At 10-day intervals, duplicate pots were filled with the soil, and planted to June clover and alfalfa. The stored samples were thoroughly mixed and aerated. The number of seedlings appearing above ground in these pots was taken to represent the germination except where no growth occurred, in which case the seeds were found in the soil and the percentage of germination determined. Germination was considered complete in 10-days, and the potted soils were air-dried and stored.

The total soluble salt content of the soils was measured by the freezing-point depression method as developed by Bouyoucos and McCool (1, 2). The acidity of the soils as expressed by pH values, was measured by electrochemical means.

The results given are the averages of the duplicate pots. The acidity and freezing-point results are those of the soils after potting, so they really were incubated 10 days longer than the table would indicate.

From these results it appears that the sulfur had little effect on the germination and early growth of the plants, except where the large applications incubated for several weeks, in which cases the growth above ground was decreased. Attention may be called to the fact that in the case of the 3000-pound 60-day

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[1] Portion of a thesis presented to the faculty of the Michigan Agricultural College in partial fulfillment of the requirements for the degree of Master of Science, June, 1924.

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sand pots, 74 per cent of the alfalfa germinated, even though none of this came through the soil; with the 3000-pound 30-day pots the germination was ·33

TABLE 1

Germination of alfalfa and clover in Coloma sand incubated for periods as indicated

SULFUR APPLIED	0 DAYS		10 DAYS		120 DAYS		30 DAYS		60 DAYS	
	C	A	C	A	C	A	C	A	C	A
None....................	94	62	84	51	89	59	91	68	88	65
500 pounds.........			89	55	82	56	84	64	91	62
1,000 pounds.........	89	62	93	58	86	55	88	65	90	62
1,500 pounds.........	90	67	91	51	89	64	89	59	78	42
2,000 pounds.........	89	55	97	54	90	59	86	57	48	51
3,000 pounds.........	88	57	90	60	94	49	5*	7*	0†	0†

A—Alfalfa.
C—Clover.

*⎰A, 33 per cent germinated but did not appear through soil.
⎱C, 61 per cent germinated but did not appear through soil.

†⎰A, 74 per cent germinated but did not appear through soil.
⎱C, 52 per cent germinated but did not appear through soil.

TABLE 2

pH values of sand incubated for periods as indicated

SULFUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS	60 DAYS
	pH	pH	pH	pH	pH
None.........................	7.95	8.2	8.15	8.2	8.05
500 pounds................	7.75	7.5	7.6	7.5	7.5
1,000 pounds..............	7.65	7.35	6.75	6.7	6.3
1,500 pounds..............	7.7	7.2	5.6	5.0	4.3
2,000 pounds..............	7.65	7.2	4.5	4.4	3.9
3,000 pounds..............	7.6	6.7	4.4	4.1	3.65

TABLE 3

Freezing-point depression of Coloma sand plus 30 per cent water

SULFUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS	60 DAYS
	°C.	°C.	°C.	°C.	°C.
None.........................	0.007	0.016	0.017	0.015	0.017
500 pounds................	0.011	0.028	0.042	0.043	0.042
1,000 pounds..............	0.034	0.037	0.043	0.043	0.047
1,500 pounds..............	0.041	0.045	0.047	0.051	0.070
2,000 pounds..............	0.041	0.043	0.058	0.060	0.080
3,000 pounds..............	0.045	0.051	0.060	0.073	0.112

per cent and the growth 7 per cent. This indicates that alfalfa seed will germinate when the intensity of the acidity is too great for growth.

The acidity of the soils and the amount of soluble material increased with the amount of sulfur applied and the length of the incubation period. There appears to be a correlation between the pH values and the amount of soluble material present, and this is more apparent in the sand cultures. The increase in soluble salts in these soil is undoubtedly due, in a large part, to the biological oxidation of sulfur.

After reaching a certain hydrogen-ion concentration, a very slight change in acidity has a decided effect on the stand. This is shown in the sand where

TABLE 4

Germination and growth on Miami silt loam

SULFUR APPLIED	0 DAYS		10 DAYS		20 DAYS		30 DAYS	
	C	A	C	A	C	A	C	A
None..................................	63	59	86	72	89	64	80	69
1,500 pounds.........................	89	62	90	64	93	60	73	63
2,000 pounds.........................	92	68	83	59	91	61	24	10
3,000 pounds.........................	86	64	74	54	70	52	2	0

TABLE 5

pH values of Miami silt loam

SULPHUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS
	pH	pH	pH	pH
None..................................	4.9	5.05	4.97	5.05
1,500 pounds.........................	4.85	4.35	3.95	3.62
2,000 pounds.........................	4.75	4.1	3.75	3.4
3,000 pounds.........................	4.75	3.5	3.4	3.16

TABLE 6

Freezing-point depressions of silt loam plus 35 per cent water

SULFUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS
	°C.	°C.	°C.	°C.
None..................................	0.011	0.019	0.017	0.021
1,500 pounds.........................	0.0215	0.042	0.0495	0.054
2,000 pounds.........................	0.023	0.051	0.076	0.085
3,000 pounds.........................	0.024	0.059	0.1045	0.1165

a fair growth occurred at pH 4.3, but practically none at pH 4.1, and in the silt loam where similar results were obtained at pH 3.5 and pH 3.4.

From the fact that growth practically ceased in the sand at pH 4.1 while in the silt loam the plants grew well at pH 3.5, it is apparent that the acidity at which a plant will grow is a property of the soil and not entirely of the plant itself, and will vary with the soil used. And it appears also that this is due to some effect on the growth of the seedling and not on germination. The hydro-

gen ion concentration produced in a soil by a certain treatment also is controlled
by the soil itself, and results on different soils will not be strictly comparable.

In the sand cultures there was better growth in the 2000-pound—60-day
pots, than in the 3000-pound—30-day pots although the former had the
greatest content of soluble salts. Similar results may be found in the silt
loam cultures. This fact would seem to indicate that the death point of
the plants was not due to too great a concentration of the soil solution.

Samples of the untreated and treated sand cultures were placed in glass cylin-
ders and leached by percolation with 5 liters of water. Samples of the leach-
ings were taken after the first 250 cc. had passed through, and also the last
250 cc. of percolate was collected in each case. These leachings were analysed
for Ca and SO_4 and the pH value was found. The hydrogen-ion concentration
of soil samples taken after $4\frac{1}{2}$ liters had passed through, also was found and
compared with the same for the unleached soils.

These figures show that although the sulfate was practically all removed by
leaching, the acidity produced by sulfur oxidation was not. On the contrary

TABLE 7

Results of leaching treated and untreated soils

	$BaSO_4$ IN 50 cc.	CaO IN 50 cc.	pH
	gm.	*gm.*	
Treated unleached soil......................			5.5
Treated leached soil.........................			5.3
First leachings.............................	0.0320	0.0085	5.6
Last leachings..............................	Trace	Trace	4.4
Untreated unleached soil.....................			7.5
Untreated leached soil.......................			6.9
First leachings.............................	0.0004	0.0010	7.5
Last leachings..............................	None	Trace	5.6

leaching made the treated soil slightly more acid. Apparently the sulfuric
acid reacted with the soil bases as fast as it was formed, and the increased soil
acidity was due to insoluble acids or acid salts. The alkaline soil was made
more acid by leaching, and the last leachings from this soil were strongly acid.

Practically all of the soluble calcium and sulfate sulfur were washed from the
soil. The untreated soil contained essentially no sulfates. Although the
untreated soil was alkaline and showed the presence of excess carbonate when
treated with acid, the first leachings from the treated soil contained more cal-
cium than those from the untreated. This shows that the treatment made the
calcium more soluble. There was some evidence that the treatment floccu-
lated the colloids present, inasmuch as the water percolated faster in the treated
soil.

Lime-requirement determinations were made on some of the treated soils
by an electrometric titration method developed by Spurway (3). The results
show that although there may be some correlation between pH value and total

lime required to bring one soil to neutrality under different conditions, yet there is no correlation between these properties in different types of soil.

Some sulfur-treated plots on Plainfield loamy sand were planted to mammoth clover, and the acidity of soil samples taken at intervals during the summer was determined. The decrease in stand of clover and the increase in acidity varied directly with the amount of sulfur applied. On one of the plots, the pH value of which was 3.1 some clover was found growing four months after treatment.

ACKNOWLEDGMENT

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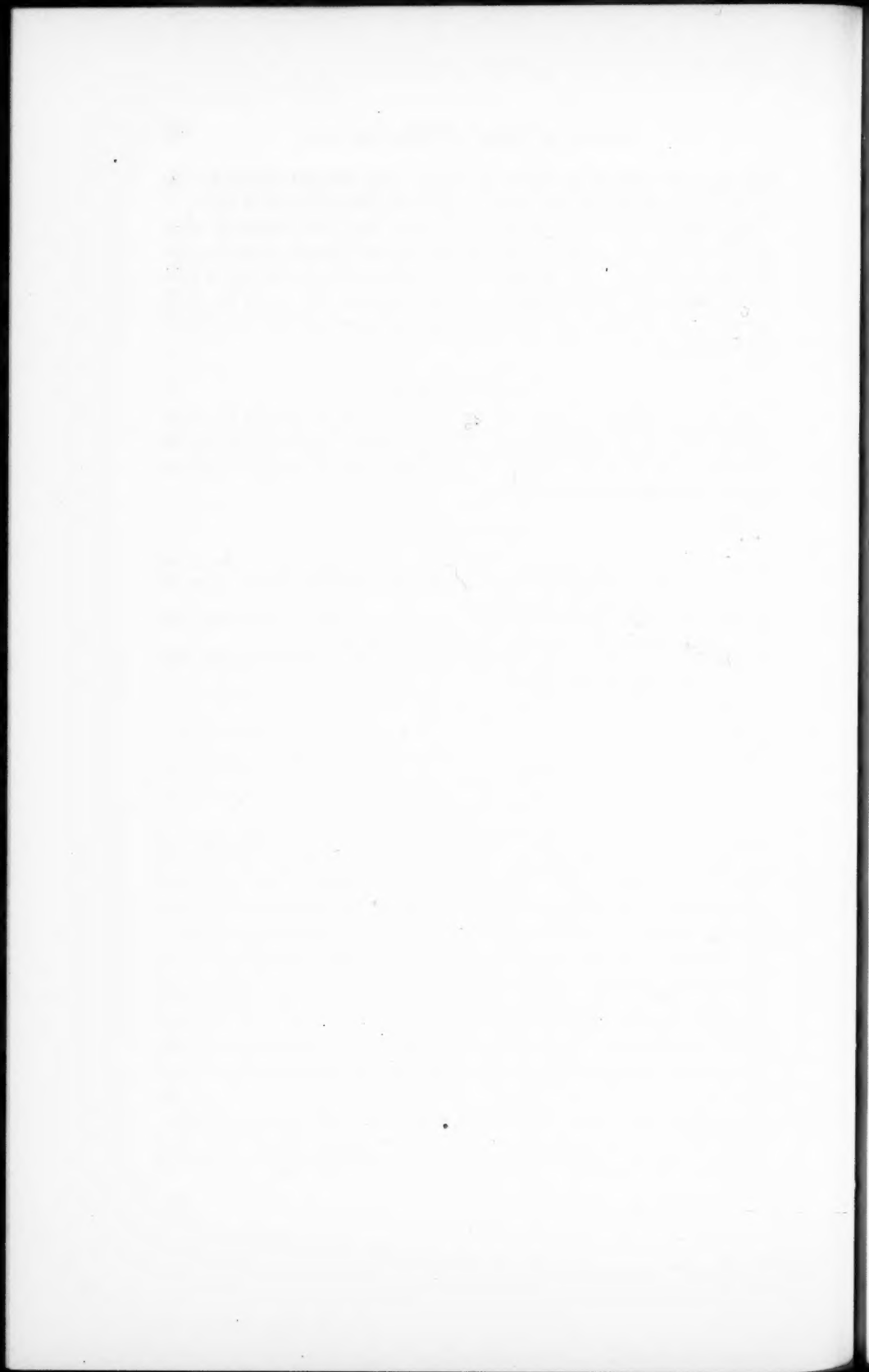
A STUDY OF SEVERAL ORGANIC SOIL PROFILES[1]

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It is rather difficult to correlate results obtained by different investigators on the nutritional, ecological and other phases in which soils are employed as the media for plant growth because of a lack of satisfactory and standardized methods of measuring the physico-chemical properties of soils. For example, the profiles of the mineral soils of northern Michigan are composed of five distinct horizons, whereas those of the southern portion of the state have usually five distinct horizons differing markedly from soils of similar texture in the north (4). Differences in the amount and nature of the materials that go to make up the organic soil profiles have been observed (2). As Dr. C. F. Marbut has brought out (3), it is desirable to study soils as such, and much greater attention should be given to the various soil horizons. The indications are that the plant is influenced not only by the surface few inches of soil but by the properties of the horizons of the entire soil profile. Thus it seems that the ecologist would find it profitable to consider more carefully the various soil horizons while carrying on field investigations.

Although reports of physical investigations on mineral soils are legion, this is not the case with respect to organic soils. In this field we find much less information, yet it is probable that the physico-chemical relationships of these soils are almost as far-reaching in their effect on plant growth, the methods of fertilizing and other phases of their management, as they are with mineral soils.

It has been found mainly through the use of mineral soils that water in soils varies tremendously with respect to the temperature relationships (1). Some of it may freeze readily when the temperature is slightly below 0°C., some may not freeze at this temperature but will solidify at or near -2°C. and some may freeze at -4°C., while some may not solidify even at much lower temperatures. The water of soils has been classified on the basis of such properties. From the physiological aspect such relationships of the soil and moisture doubtless are of tremendous importance.

It is well recognized that dry soils when moistened give off heat and the number of calories of heat evolved varies considerably with different soils. Apparently the colloidal content and the state of the colloidal material has a great effect upon this phenomenon.

It has long been known that wet peat shrinks markedly upon drying and this property is important from both the agricultural and the industrial standpoint. When organic deposits are drained it is possible that the degree of such shrinkage has an important bearing upon this practice.

It has occurred to us that these phenomena may be utilized in studying the physical properties of organic soils and perhaps assisting in their classification.

EXPERIMENTAL RESULTS

Dilatometer studies

It is possible, we found, during the progress of our investigations, that the water content of the soil used in dilatometer studies regulates somewhat the results obtained. Accordingly, dry materials were sampled in triplicate and treated with different amounts of water, well mixed, and allowed to stand in the moist condition two days before making the determinations.

Several samples were taken from the field and used in the moist condition. That is, they were not permitted to become air-dry before studies were made. One portion of each sample was placed in a closed container where it remained unchanged so far as moisture content was concerned, another portion was allowed to lose some moisture by evaporation and a third portion was permitted to lose still more.

It was considered important also to determine whether or not the air-drying of samples of organic soils results in a measurable change in the results obtained from dilatometer studies. For this purpose samples were brought from the fields, thoroughly mixed while wet, separated into two portions and their weights recorded. One portion was permitted to lose moisture by evaporation until it became air-dry, and then was made up again to the original weight with water before the studies were undertaken. According to the results presented in table 1 the amount of water that fails to freeze in the materials used is practically the same where the total water content is about the same, and air-drying does not affect the results obtained. Additional results are presented in conjunction with the heat of wetting studies.

A brief description of these materials and also of the materials mentioned in tables 3 and 4, is given in table 5.

Heat of wetting

It was brought out early that there is an appreciable difference in the time required for different materials to reach equilibrium when moistened (or to cease to generate heat upon becoming wet). It was apparent that if some samples were worked up at the proper moisture content and left in a porous condition they took up water readily, whereas if collected while quite wet and permitted to dry without being broken up they became very hard and relatively impervious, and even when crushed to very small particles took it up very slowly as indicated by the rate at which they generate heat.

TABLE 1

Unfree water held at different water contents

SAMPLE AND TREATMENT	WATER CONTENT	WATER HELD UNFREE PER 10 GM. OF OVEN-DRY MUCK
	per cent	*cc.*
Bope, 1st foot, air-dried	101.06	4.94
Bope, 1st foot, air-dried	123.98	4.99
Bope, 1st foot, air-dried	152.85	5.13
Bope, 2nd foot, air-dried	113.41	5.84
Bope, 2nd foot, air-dried	169.60	6.49
Bope, 2nd foot, air-dried	203.63	7.05
Town Line, surface, air-dried	125.27	5.54
Town Line, surface, air-dried	184.55	6.11
Town Line, surface, air-dried	188.80	6.00
Farm Lane, surface, air-dried	125.96	4.83
Farm Lane, surface, air-dried	183.57	5.49
Farm Lane, surface, air-dried	201.37	5.48
Town Line, surface, kept moist	121.58	5.63
Town Line, surface, kept moist	166.38	6.04
Town Line, surface, kept moist	191.45	6.27
Town Line, subsoil, kept moist	232.84	7.87
Town Line, subsoil, kept moist	346.15	8.36
Town Line, subsoil, kept moist	409.54	8.88
Farm Lane, surface, kept moist	128.86	5.57
Farm Lane, surface, kept moist	159.75	5.90
Farm Lane, surface, kept moist	179.93	6.22
Farm Lane, subsoil, kept moist	223.62	7.85
Farm Lane, subsoil, kept moist	335.58	8.39
Farm Lane, subsoil, kept moist	369.32	8.63
Town Line surface, dried and rewet	153.50	5.76
Town Line surface, kept wet	153.19	5.92
Town Line subsoil, dried and rewet	297.84	8.04
Town Line subsoil, kept wet	301.99	8.13
Farm Lane surface, dried and rewet	185.45	5.74
Farm Lane surface, kept wet	152.35	5.48
Farm Lane subsoil, dried and rewet	302.65	8.41
Farm Lane subsoil, kept wet	294.04	8.28

It was therefore thought advisable to determine the effect of the physical condition of the materials on the rate at which heat is generated. Some of the less pervious materials, or those that become very hard upon drying, taken from the third and fourth foot of a deposit, were used for these investigations. They were ground to different degrees of fineness and the heat of wetting determined.

Two samples mentioned above were used for this work and the operation was repeated twice with a slight change in the method. (A) In the first case the material was crushed to pass through a 3-mm. sieve. It was then divided in two equal parts, one being used to determine the heat of wetting without further change, while the other was quite finely ground without crushing the particles too much before using. (B) In the second case the material was crushed to pass a 3-mm. sieve, then it was sifted through a 2-mm. sieve and that which passed through was rejected, nothing being used except the lumps ranging in size from 2 to 3 mm. This material was divided into two equal

TABLE 2

Effect of physical condition on the heat of wetting

| TREATMENT | DEPTH OF SAMPLE | | | |
| | Third foot | | Fourth foot | |
	Not ground	Ground	Not ground	Ground
Method A:				
Time (minutes).........................	42	8	46	8
Heat of wetting (calories)................	760.50	784.40	711.08	728.50
Method B:				
Time (minutes).........................	55	11	75	15
Heat of wetting (calories)................	738.90	760.00	675.00	695.00

parts, one of which was ground before being used. The results of this work are given in table 2.

The striking thing about these results is the great difference in the time required for materials of different fineness to generate the total heat upon being placed in water. It was observed that in case of the ground samples the most of the heat was produced in the first minute and the amount produced in each succeeding minute was less until the maximum was reached in 8 to 12 minutes. This indicates that the very fine material took up moisture readily and the small amount of slightly coarser material took up moisture more slowly. In the case of the unground soil, which ranged in size of lumps from very find up to 3 mm., the per cent of total heat produced in the first minute was much less, and for the material ranging from 2 to 3 mm. it was still smaller.

The heat of wetting of samples taken at different depths from several deposits also was determined. Thin slabs were cut from each and thoroughly mixed, while still moist, before using. The time required for those taken from several

TABLE 3

Loss on ignition, heat of wetting per 25 gm. of soil, and time required for soils to reach maximum temperature in heat of wetting

SAMPLE	LOSS ON IGNITION	HEAT OF WETTING PER 25 GM. OF MATERIAL	TIME REQUIRED TO REACH EQUILIBRIUM
	per cent	*calories*	*minutes*
Bope:			
1st foot	65.8	766.6	8
2nd foot	83.1	787.5	12
3rd foot	85.7	700.8	13
4th foot	57.9	569.7	6
5th foot	47.2	506.5	6
6th foot	17.0	185.2	5
De Camp:			
1st foot	81.0	954.5	5
2nd foot	85.3	933.9	7
3rd foot	87.3	900.6	3
4th foot	87.5	904.1	11
5th foot	85.6	838.1	7
Homer:			
1st foot	84.0	901.3	8
2nd foot	89.3	847.7	12
3rd foot	76.9	708.3	15
4th foot	80.5	744.6	13
Thorp:			
1st foot	84.8	846.4	8
2nd foot	86.9	884.0	5
3rd foot	89.6	815.5	4
4th foot	89.2	716.9	8
Hudsonville:			
1st foot	80.5	916.0	5
2nd foot	85.8	853.0	8
3rd foot	83.8	821.0	11
Kingery:			
0–5 inches	72.7	692.0	14
5–8 inches	85.2	636.0	12
8–16 inches	86.2	628.0	7
16–24 inches	84.5	631.0	12
24–32 inches	78.5	635.0	9
Ingham County[1]:			
0–6 inches	78.3	457.7	
6–24 inches	72.4	456.6	
24–40 inches	82.3	341.0	

TABLE 3—*Continued*

SAMPLE	LOSS ON IGNITION	HEAT OF WETTING PER 25 GM. OF MATERIAL	TIME REQUIRED TO REACH EQUILIBRIUM
	per cent	*calories*	*minutes*
Ingham County[a]:			
0–15 inches............................	81.2	722.0	
15–36 inches...........................	85.8	751.0	
Posen:			
0–4 inches............................	80.1	769.7	
4–24 inches............................	83.5	778.4	
24–36 inches...........................	88.3	788.8	
36–48 inches...........................	66.1	564.0	

TABLE 4

Unfree water, heat of wetting, and loss on ignition of surface materials

SAMPLE NUMBER	UNFREE WATER	HEAT OF WETTING PER 25 GM. OF MATERIAL	LOSS ON IGNITION	RATIO OF HEAT OF WETTING TO UNFREE WATER
	per cent	*calories*	*per cent*	
3	41.2	397.32	89.7	9.6
1	46.2	477.53	92.6	10.3
2	49.2	463.77	90.4	9.4
20	49.3	486.67	56.9	9.8
12	52.4	466.97	85.8	8.9
17	55.2	596.86	71.8	10.8
13	56.0	552.95	72.7	9.8
16	60.0	529.72	75.4	8.8
7	61.4	559.22	74.8	9.1
5	61.5	579.28	75.6	9.4
18	61.5	564.92	76.9	9.1
11	62.3	664.44	76.3	10.6
19	63.5	697.48	82.2	10.9
4	64.2	670.46	79.0	10.4
6	64.6	647.99	76.2	10.0
8	66.5	646.07	79.0	9.7
14	66.5	693.20	83.5	10.4
9	69.5	666.52	80.7	9.5
10	70.9	714.32	78.8	10.0
15	70.9	708.42	84.2	9.9

* In making these determinations 5 gm. of air-dry soil was moistened with 5 cc. of H_2O.

deposits to reach the maximum temperature, as well as the heat of wetting and the loss on ignition, is given in table 3. It seems that the best method of preparing the samples is to work them up with the hands when at the proper moisture condition, so that they will dry out to be granular and porous. Even with this treatment some of them are more or less resistant to wetting as the data in table 4 show.

TABLE 5

A brief description of materials mentioned in tables 1, 3 and 4*

SAMPLE NUMBER OR NAME	COLOR	TEXTURE	VEGETATION
1	Brown	Coarse	Huckleberry
2	Brown	Coarse	Huckleberry
3	Brown	Coarse	Huckleberry
4	Dark brown	Finely divided	Tamarack
5	Dark brown	Finely divided	Tamarack
6	Dark brown	Finely divided	Cat tail
7	Brown	Finely divided	Huckleberry
8	Black	Finely divided	Tamarack
9	Black	Finely divided	Tamarack
10	Dark brown		
11	Dark brown		
12	Brown	Coarse	Huckleberry
13	Black	Finely divided	Black ash and elm
14	Dark brown	Medium fine	
15	Dark brown	Coarse	
16	Black	Finely divided	
17	Black	Finely divided	
18	Dark brown	Finely divided	
19	Black	Finely divided	
Town Line:			
Surface....................	Black	Finely divided	
Subsoil....................	Black	Finely divided	
Farm Lane:			
Surface....................	Black	Finely divided	
Subsoil....................	Dark brown	Slightly fibrous	
Bope:			
1st foot....................	Dark brown	Finely divided	
2nd foot...................	Dark brown	More woody	
3rd foot...................	Dark brown	Woody	
4th foot...................	Dark brown	Woody	
5th foot...................	Gray tinge	Sandy	
6th foot...................	Gray	Quite sandy	
DeCamps:			
1st foot....................	Brown	Coarse	
2nd foot...................	Brown	Woody	
3rd foot...................	Brown	Woody	
4th foot...................	Brown	Woody	
5th foot...................	Brown	Woody	

* The soils described in this table are the only ones in this article referred to by these numbers. Wherever "No. 1" appears it means the same soil. The same is true of "Town Line" or "Hudsonville," etc.

TABLE 5—*Continued*

SAMPLE NUMBER OR NAME	COLOR	TEXTURE	VEGETATION
Homer:			
1st foot....................	Dark brown	Finely divided	
2nd foot...................	Dark brown	Slightly woody	
3rd foot...................	Dark brown	Slightly woody	
4th foot...................	Dark brown	Slightly woody	
Thorpe:			
1st foot....................	Dark brown	Finely divided	
2nd foot...................	Brown	Slightly fibrous	
3rd foot...................	Brown	Slightly fibrous	
4th foot...................	Brown	Slightly fibrous	
Hudsonville:			
1st foot....................	Black	Finely divided	
2nd foot...................	Dark brown	Slightly woody	
3rd foot...................	Dark brown	Slightly woody	
Kingery:			
1st foot....................	Black	Finely divided	
2nd foot...................	Black	Slightly coarser	
3rd foot...................	Black	Slightly coarser	
Ingham County[1]:			
0–6 inches..............	Dark brown	Finely divided	
6–24 inches..............	Brown	Slightly coarser	
24–40 inches..............	Brown	Somewhat woody	
Ingham County[2]:			
0–15 inches..............	Dark brown	Finely divided	
15–36 inches..............	Brown	Somewhat coarser	
Posen:			
0–4 inches	Brown	Coarse	
4–24 inches..............	Brown	Coarse	
24–36 inches..............	Brown	Woody	
36–48 inches	Dark grayish brown	Fine, colloidal	

Additional studies were made with respect to the heat of wetting and unfree water of samples taken from the first foot of numerous deposits. The color, texture and vegetation are given in table 5. The data in table 4 show the relationship between the heat of wetting, the per cent of water that fails to freeze on the oven-dry basis, and loss upon ignition. The materials are arranged according to the ascending order of the per cent of water that failed to freeze. The heat of wetting and the loss upon ignition also are given.

TABLE 6

Moisture content and shrinkage of organic soil profiles

NAME OF DEPOSIT	DEPTH OF SAMPLE	WATER TABLE	WATER BY WEIGHT	WATER PER CUBE	APPARENT	SHRINKAGE
	inches	*inches*	*per cent*	*gm.*	*sp. gr.*	*per cent*
Thorp's...........	0–4		143.1	418.5	0.28	33.02
	12–16		384.4	673.5	0.17	50.50
	24–28		577.9	887.0	0.15	78.03
	30–34		692.7	906.8	0.12	70.47
	36–40		653.7	928.2	0.13	80.47
	48–52		556.8	907.1	0.15	61.41
Chandlers.........	0–4		147.8	511.0	0.33	33.00
	12–16		466.5	833.5	0.17	68.36
	24–28	36	487.7	908.1	0.18	78.03
	36–40		860.6	947.5	0.10	75.87
	48–52		826.6	929.8	0.14	80.25
Trowbridge.......	0–4		110.6	460.0	0.40	23.09
	6–10		479.7	880.2	0.17	78.03
	12–16	30	616.2	901.3	0.14	78.03
	24–28		898.1	950.2	0.10	58.17
	36–40		1333.8	941.4	0.07	64.84
	48–52		1183.3	972.7	0.08	70.19
South Farm.......	0–4		126.1	320.5	0.24	33.0
	12–16		530.7	758.3	0.14	61.33
	24–28	30	555.5	864.3	0.15	69.05
	36–40		691.6	924.1	0.13	70.45
	48–52		742.5	939.2	0.12	61.33
Valleau..........	0–4		139.4	367.1	0.25	28.33
	8–12		392.2	663.5	0.16	63.16
	12–16		500.9	720.7	0.14	64.61
	24–28	72	748.6	792.7	0.10	56.30
	36–40		734.5	914.4	0.12	59.64
	48–52		933.2	951.8	0.10	56.30
	60–64		912.7	948.3	0.10	54.56
Shaw's..........	0–4		83.1	366.7	0.42	23.09
	6–10		274.9	654.9	0.23	50.50
	12–16	.	483.3	825.9	0.16	61.41
	24–28		719.1	931.2	0.12	84.19
	36–40		611.4	934.2	0.15	81.19
	48–52		325.0	886.0	0.26	78.03
Town Line........	0–4		82.3	335.5	0.39	33.00
	6–10		292.3	716.7	0.23	66.28
	12–16	39	401.8	829.2	0.20	73.19
	24–28		697.2	937.0	0.13	66.28
	36–40		744.5	965.6	0.12	83.90
	48–52		355.2	918.3	0.25	57.21

TABLE 6—*Continued*

NAME OF DEPOSIT	DEPTH OF SAMPLE	WATER TABLE	WATER BY WEIGHT	WATER PER CUBE	APPARENT	SHRINKAGE
	inches	*inches*	*per cent*	*gm.*	*sp. gr.*	*per cent*
	0–4		134.7	565.3	0.40	33.00
	6–10		246.2	698.8	0.27	46.37
	12–16		432.0	716.3	0.16	54.37
Farm Lane........	24–28		646.4	919.2	0.14	56.34
	36–40		675.6	925.6	0.13	56.34
	40–44		821.8	931.0	0.11	78.03
	48–52		1069.0	976.9	0.09	80.47

The results seem to show that the heat of wetting and the unfree-water-holding capacity of organic soils are dependent not entirely upon the organic content but upon the state of decomposition and nature of the materials. Soils 1, 2 and 3 have a very high organic-matter content and their heat of wetting and unfree-water-holding capacity are rather low, while 20, 13 and 17 are among those of lowest volatile matter content and have an unfree-water-holding capacity and heat of wetting slightly greater than those of 1, 2 and 3. Furthermore, soil 15, which has the highest unfree-water-holding capacity and next to the highest heat of wetting, has a very high organic matter content.

SHRINKAGE UPON DRYING.

The samples utilized for the accumulation of data on the volume weight and shrinkage upon drying were taken by excavating to the desired depth and sampling with a galvanized iron cube open on one side. The cube was carefully inserted into the various sections of the deposits, and removed, the contents weighed and oven-dried, and the measurements taken. The materials were collected August 1, at a time when the surface layers were not very high in water content. The results of these investigations are presented in table 6. A few of the cubes after drying are shown in plate 1.

It is to be noted that in nearly all cases the cubes taken from the surface layers practically retained their cubical shape on being dried. They shrank somewhat but the vertical shrinkage was about the same as the horizontal shrinkage. In case of the samples taken below the surface the horizontal shrinkage was less than the vertical. The greatest change in volume was found to take place in the layers of very fine and somewhat colloidal material, while a medium shrinkage occurred in the more fibrous layers. In addition, the vertical shrinkage in proportion to the horizontal shrinkage was greatest in the fibrous layers. The apparent specific gravity of the cubes as removed from the field was determined, and was found to be the greatest in case of the first section sampled.

SUMMARY

1. The amount of water an organic soil contains has some influence on the amount it will hold unfree, the latter being greatest where the water content is high. Air-drying a soil and wetting it again has no effect on the amount of water it will hold unfree, provided the soil is allowed to become thoroughly moist before the determination is made.

2. The physical condition of organic soils has a great influence on the rate at which they will take up water. A fine-textured organic soil that is removed from the deposit while wet and allowed to dry in large chunks will take up water very slowly. · This is especially true of the lower horizons of fine-textured materials. This physical condition has no influence on the amount of heat generated on wetting but it does have an influence on the rate at which heat is developed.

3. There is a very close relationship between the heat of wetting and the unfree-water-holding capacity of organic soils. It seems, however, that the ability of organic soils to develop heat upon becoming wet and to hold water unfree is dependent not upon the organic content of the soil but upon the stage of decomposition and nature of the materials. A soil with a very low organic content, such as is found at or near the bottom of some organic deposits, naturally has a low heat of wetting due to its mineral content; but, as a rule, the sections near the middle of the profile where the organic content is highest give less heat of wetting than those at the surface where the organic content is somewhat lower, but is usually more thoroughly decomposed.

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PLATE 1

FOUR-INCH CUBE OF ORGANIC SOIL, AFTER DRYING, TAKEN AT DEPTH INDICATED BELOW
EACH CUBE

The 4-inch cube sample is shown at the left in each figure.

FIG. 1. Cubes taken from Farm Lane deposit.   Note depth of greatest shrinkage at 40–44
inches near the bottom of the deposit.

FIG. 2. Cubes taken from Thorp's deposit.   Here a thin layer of fibrous material is found
at 32 inches between two layers of colloidal material.

FIG. 3. Cubes taken from Shaw's deposit.   The depth of colloidal material or of greatest
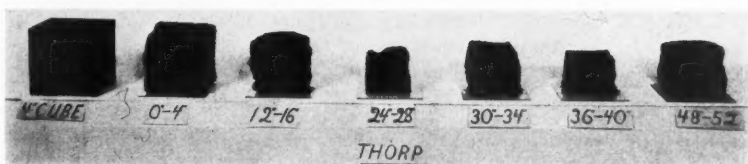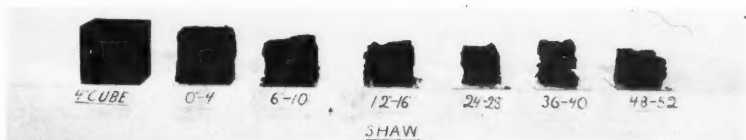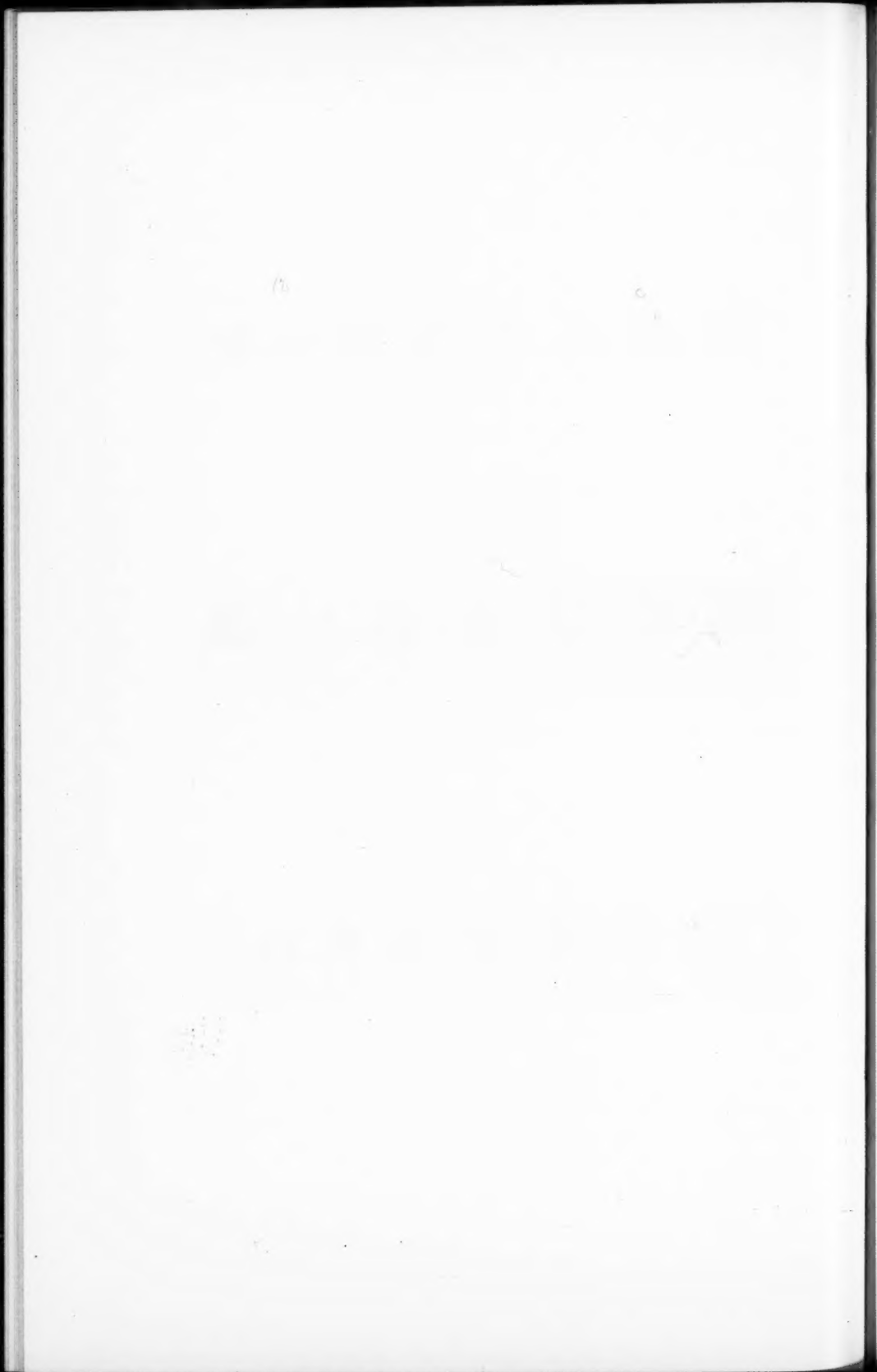shrinkage is found between 20 and 44 inches.

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FIG. 1

FIG. 2

FIG. 3

NOTE ON THE ABSORPTION OF BASES BY SOILS

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It has for some time been regarded as an established fact that, all other things being constant, the greater the concentration of a base in solution the greater is the amount absorbed by a soil in contact with the solution. In a recent paper by C. P. Jones (1), however, it is claimed that beyond a certain concentration "an increase in concentration results in a decrease in absorption." As the mechanism of the absorption of bases by soils is so important and attractive a subject, it seems most desirable that such a challenge of a hitherto accepted fact of the problem as that made by Jones should be most carefully and critically considered. In this note, the writers wish to submit that Jones' deductions are invalid and that his experimental data cast no doubt whatever upon the accepted belief that the amount of base absorbed from solution by soils increases with concentration of the base.

Jones agitated solutions of suspensions of carbonates and bicarbonates of alkali and alkaline-earth metals with soil, and determined the amount of carbon dioxide liberated. The amount of carbon dioxide liberated was taken as a measure of the amount of carbonate decomposed and therefore of the amount of base absorbed. The following are his results with solutions of sodium carbonate and bicarbonate and an unlimed soil:

	Na_2CO_3										$NaHCO_3$	
Concentration of carbonate	$0.01M$	$0.02M$	$0.03M$	$0.04M$	$0.05M$	$0.06M$	$0.10M$	$0.20M$	$0.50M$	Saturated	$0.06M$	$0.12M$
CO_2 from 10 gm. soil (mgm.)...	3.7	4.6	4.4	4.4	4.3	2.4	1.1	1.0	0.7	0.3	15.3	19.7

Now in the experiments with the normal carbonate, it seems obvious that the carbon dioxide formed by the reaction with the soil will not be wholly evolved as gas, but will react with the remaining carbonate to form bicarbonate. That carbon dioxide does so react with the carbonates of alkali and alkaline-earth metals is a familiar fact, and the conditions under which the carbon dioxide is formed in these experiments will clearly conduce to the quantitative attainment of the reaction. Also the greater the concentration of the carbon-

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ate, the greater will be the tendency for the solution to retain the carbon dioxide. The falling off in the amount of carbon dioxide evolved as the concentration of the carbonate increases is held by the present writers to be due to bicarbonate formation and not, as Jones assumes, to a falling off in the amount of base absorbed and in the amount of carbon dioxide actually formed in the primary reaction. The far greater amount of carbon dioxide evolved when sodium bicarbonate was used (attributed by Jones to a greater hydrolysis of the bicarbonate) is in full accordance with this view.

Using as far as possible the technique described by Jones, the following experiments were carried out. The results support the criticism which is here submitted.

1. A slow current of air was drawn by means of a pump through 50 cc. of saturated potassium bicarbonate solution and thence into 50 cc. of saturated lime-water. A similar current was drawn at the same time by the same pump through 50 cc. of an equivalent solution of potassium carbonate and thence into 50 cc. of lime-water. After 2 hours it was found that the current passed

TABLE 1

Potassium absorbed by 10 gm. soil

SOIL	FROM K_2CO_3		FROM $KHCO_3$	
	Calculated from CO_2 evolved	Calculated from titration	Calculated from CO_2 evolved	Calculated from titration
	mgm.	*mgm.*	*mgm.*	*mgm.*
A heavy sour soil......................	0.30	33.40	43.90	40.40
A sour loam............................	0.35	66.65	53.79	62.95
An acid-extracted soil.................	0.07	518.00	*	580.00

* The amount of CO_2 evolved here was more than sufficient to saturate the lime-water used.

through the bicarbonate had completely carbonated the lime-water, while that which had passed through the carbonate solution had carbonated only 1 per cent of the lime-water.

2. Fifty-gram portions of a sour soil were treated respectively with saturated potassium bicarbonate and an equivalent solution of potassium carbonate. The carbon dioxide evolved was collected in lime-water and estimated. Also the solutions were filtered at the end of the experiment, and the amount of base absorbed was estimated by titration. The results are given in table 1.

It seems abundantly clear therefore that the amount of carbon dioxide *evolved* when normal alkali carbonates react with soil is no measure at all of the amount of base absorbed.

REFERENCE

(1) JONES, C. P. 1924 Adsorption and absorption of bases by soils. *In* Soil Sci., v. 17, p. 255–273.

ALKALI SOIL INVESTIGATIONS: III. CHEMICAL EFFECTS OF TREATMENTS[1]

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Any treatment of alkali soils, as previously pointed out (6), must involve, among other things, the replacement of the bases in the zeolitic portion of the soil and the creation of a reaction favorable for plant growth. By improving the physical condition of the alkali soil, as outlined previously (5, 6), the leaching operations are facilitated. This in turn must have an effect on the replacement process, since the presence of large amounts of the soluble salts hinders the interreaction of the ameliorating agent with the replaceable zeolitic cations.

Table 1 gives the scheme of treatments used in the first series of experiments. Flower pots, of 1.4 pounds capacity, were used in studying the effects of various treatments in combination with leaching operations. Large earthenware glazed pots were used for studying the effects of the various treatments without leaching. The flower pots were paraffined to prevent absorption. It was found later that this treatment did not accomplish the purpose and some salts, especially potassium were absorbed by the clay walls.

From time to time a number of small pots were taken to the laboratory and leached. The purpose was to study the effects of the various treatments on the leaching capacity of the soil. At the same time analyses of the leachings were made to determine the changes produced by the treatments. In the series of experiments reported, tap water was used for leaching, with the thought that such water would correspond more closely to irrigation conditions. The procedure was as follows:

Each pot received a total of 400 cc. of water; the water was allowed to be in contact with the first two samplings (taken after 14 days and 48 days) for an indefinite period of time, and the rate of percolation was followed. Later a definite period of time, 48 to 72 hours, of contact was used, after which the water from the surface was poured off. The leachings were measured and then made up to 250 cc. In cases where the leachings amounted to more than 250 cc. they were made up to 300 cc.

Simultaneously with the leaching of the small pots, samplings were made from the large pots. Fifty grams of soil were mixed with 500 cc. of distilled

water, shaken occasionally for three hours, left over night, centrifuged for
one and one half hours and analyzed in the same manner as the leachings.

Hibbard (4) has shown that water extracts do not represent the true con-
dition in the soil. The displacement method which is supposed to represent
the actual soil solution shows that carbonates, bicarbonates and phosphates

TABLE 1

Treatment of alkali soils, first series

LABORATORY NUMBER	TREATMENT
1	None
2	4000 lbs. sulfur
3	4000 lbs. sulfur + 5 tons peat
4	6000 lbs. sulfur
5	6000 lbs. sulfur + 5 tons peat
6	2000 lbs. sulfur
7	2000 lbs. sulfur + 5 tons peat
8	4000 lbs c.p. alum + 5 tons peat
9	4000 lbs. c.p. alum + 2000 lbs. sulfur
11	5 tons peat

TABLE 2

Analyses of leachings from pots incubated 14 days: first series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL								
		C as CO_2	C as HCO_2	C as organic carbon leached out as C*	Cl	Ca	Mg	P as phosphates	S as sulfates	N
	cc.									
1	188	27.8	107.6	84.9	2204.6	40.9	6.3	9.4	486.9	10.8
2	168	0.0	24.1	38.8	2184.9	114.9	8.3	11.4	604.6	5.6
3	160	0.0	23.6	118.4	2362.1	133.8	6.9	11.9	826.7	12.7
4	159	0.0	37.4	41.5	2440.0	111.8	5.8	11.4	776.3	7.8
5	195	0.0	29.4	170.8	2303.0	163.7	8.2	12.9	855.0	13.2
6	182	Traces	71.5	49.2	2365.2	53.5	3.9	12.9	677.1	9.3
7	175	0.0	67.7	182.9	2420.6	55.1	3.5	15.7	676.5	18.3
8	180	4.2	84.3	66.1	2244.0	36.2	2.8	3.6	659.8	9.3
9	225	0.0	49.1	154.0	2362.1	132.2	6.5	3.4	941.6	7.2

*Organic carbon was determined by subtracting the sum of carbonate and bicarbonate
carbon from the total determined by the wet combustion method, with permanganate and
sulfuric acid.

are over-estimated; thus the water extract considerably misrepresents the
actual conditions in an alkali soil. The point is well taken, but solubility
studies of the constituents would reveal exactly the same story. The ex-
tracts do not represent the true condition for the reason that the hydrogen
ions of water as shown (6) have a high coefficient of energy of absorption

and they replace other cations.   We should therefore expect that by replacing sodium with hydrogen more sodium carbonate and bicarbonate would be formed.   The purpose of our analyses is to compare the effect of the products of sulfur oxidation and of other treatments on the exchange of ions in the alkali soils under uniform methods of experimentation.   Taking the

TABLE 3

Analyses of alkali soil extracts after 14 days incubation: first series

LABORA-TORY NUMBER OF TREAT-MENT	PARTS PER MILLION IN DRY SOIL									
	C as CO_3	C as HCO_3	Cl	SiO_2	Ca	Mg	P as phos-phates	Iron and alumi-num as oxides	S as sulfates	Reac-tion
										pH
1	26.4	384.7	3500	.....	.....	.....	59.1	.....	608.0	9.0
2	Trace	200.3	3239	798	319.5	182.6	74.5	219.2	1025.0	8.0
3	0.0	188.1	3239	598	435.6	182.6	62.3	219.2	996.8	8.0
4	0.0	160.6	3497	159.6	420.2	213.2	34.8	338.8	1119.0	8.0
5	0.0	137.1	3497	478.2	459.6	174.0	57.2	139.5	1250.0	8.0
6	6.0	199.8	3239	438.5	379.8	139.2	56.4	338.8	952.2	8.2
7	5.9	251.0	3239	478.7	359.5	.....	.....	219.2	912.0	8.2
8	12.1	219.3	2990	217.9	299.8	147.8	69.7	259.0	874.0	8.2
9	0.0	148.6	3239	239.3	399.6	156.6	49.4	139.5	1217.0	8.0
11	6.0	375.1	3239	1275.0	459.6	174.0	54.1	949.8	594.9	9.0

TABLE 4

Analyses of leachings from pots after 48 days incubation: first series

LABORA-TORY NUM-BER OF TREAT-MENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL									
		C as CO_3	C as HCO_3	Cl	SiO_2	Ca	P as phos-phates	K	Na	S as sulfates	Reac-tion
	cc.										pH
1	102	36.5	125.6	1984	3.8	24.6	17.0	117.6	1934	380.3	9.0
2	260	0.0	38.5	1866	20.8	191.8	10.7	100.0	2011	657.0	8.0
3	125	1.2	55.3	1984	11.3	113.5	5.0	.....	....	859.8	8.4
4	262	0.0	35.7	2055	31.2	185.2	6.9	117.2	2290	1092.0	8.0
5	312	0.0	31.1	2362	17.6	293.2	7.1	110.1	2486	1130.0	8.0
6	158	0.9	38.3	1653	12.3	88.8	8.3	93.5	1759	599.3	8.4
7	142	0.6	41.1	2614	14.2	85.0	11.3	98.7	2497	757.8	8.2
8	230	7.9	83.1	1960	10.4	37.8	14.8	159.7	1896	444.3	8.6
9	265	0.6	45.5	1866	9.4	154.0	7.7	138.4	2214	884.2	8.4
11	78	14.6	110.3	1771	14.2	32.1	11.3	70.4	1760	370.7	8.8

same amount of soil and water we get a picture of the transformations due to the treatment.   The leachings aid in bringing out the details of the picture.

In comparing data of the leaching with that of the extracts the following is to be remembered.   When a soil extract is made and then filtered through paper, the filtrate will as a rule be turbid if the particular soil has colloids,

as is the case with the alkali soils. However, the same soil when leached
gives a perfectly clear liquid. The latter is nothing more than the filtrate

TABLE 5

Analyses of alkali soil extracts after 60 days' incubation: first series*

LABORA-TORY NUMBER OF TREAT-MENT	PARTS PER MILLION IN DRY SOIL									
	C as CO_3	C as HCO_3	Cl	SiO_2	Ca	Mg	P as phos-phates	Fe and Al as oxides	S as sulfates	Reac-tion
										pH
1	15.7	371.3	1998.3	2133.7	479.5	335.5	40.4	1858.1	407.8	8.8
2	0.0	138.2	2121.1	398.4	601.5	196.0	48.0	499.1	1159.0	7.7
3	0.0	148.3	1499.1	377.9	601.5	248.8	52.9	299.9	921.2	7.2
4	0.0	139.2	......	198.4	640.9	213.5	50.5	239.3	1207.8	7.2
5	0.0	124.7	2373.1	359.0	741.7	227.7	51.4	359.0	2234.5	7.3
6	0.0	212.2	2617.2	338.5	439.6	196.0	....	299.1	1007.8	7.7
7	0.0	207.8	2373.1	557.4	479.5	226.7	50.5	459.8	1081.8	7.7
8	Traces	266.7	1499.1	359.0	419.6	234.6	52.9	259.8	511.7	8.6
9	0.0	139.5	2247.1	377.9	479.5	209.4	48.0	198.4	1373.1	7.3
11	9.8	381.0	1998.3	977.9	439.6	274.9	65.3	951.1	503.9	8.8

*Consider absorption by walls of various pots. Note the SiO_2 in alum treatment.

TABLE 6

Analyses of leachings from pots after 95 days' incubation: first series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL											
		C as CO_3	C as HCO_3	Cl	SiO_2	Ca	Mg	P as phosphates	K	Na	S as sulfates	N	Reaction
	cc.												*pH*
1	75	31.0	113.3	1770.0	11.3	18.8	11.1	4.25	94.9	1295.2	335.4	10.7	8.8
2	285	0.0	26.7	1330.6	26.4	151.1	30.5	1.73	110.0	1262.9	584.2	9.1	7.7
3	298	0.0	28.3	2210.9	29.2	198.8	45.6	4.25	111.9	1253.4	1162.9	11.0	7.6
4*	290	0.0	21.7	1307.0	41.5	203.1	59.5	1.88	47.2	1338.5	1083.4	8.9	7.4
5	293	0.0	24.2	1588.9	30.2	196.0	56.0	5.66	106.2	1272.3	1203.1	8.1	7.2
6	90	0.0	26.7	1818.7	9.4	64.2	27.8	1.10	77.9	1269.2	727.5	7.0	7.7
7	150	0.0	48.8	1620.4	17.9	81.3	26.9	2.83	102.5	1262.9	820.4	10.3	7.6
8	138	8.3	91.3	1384.1	73.6	35.9	17.3	9.29	81.7	1299.1	481.8	10.3	8.6
9	210	0.0	38.4	2527.4	12.2	96.3	42.5	.....	144.5	1195.2	1182.6	7.8	7.4
11	53	8.5	43.4	1218.8	16.0	21.7	10.2	4.40	68.5	1300.7	203.1	12.4	8.4

*The paraffin from this pot was destroyed and some of the salts passed through the walls. This will account for some discrepancies in the determinations; note the retention of K by the porous walls of the pot.

of the extract, differing only by the kind of filter used: in the extract the
filter paper is the filter, while in the leachings the soil is the filter. In the
latter case the mechanical absorbing capacity of the soil plays its part. The

data on the leachings furnish much evidence in this respect. Especially is this true in connection with the colloids such as the silicates.   Tables 2 to 10

TABLE 7

Analyses of alkali soil extract after 95 days, incubation: first series

LABORATORY NUMBER OF TREATMENT	PARTS PER MILLION IN DRY SOIL										
	C as HCO₃*	Cl	SiO₂	Ca	Mg	P as phosphates	K	Na	S as sulfates	N	Reaction
											pH
1	457.7	3036.0	1758.0	218.8	270.5	56.6	321.0	3576.2	737.2†	105.8	8.2
2	122.8	2947.9	159.0	760.5	170.0	7.8	321.0	3963.6	1944.8	57.0	7.4
3	106.7	3746.3	149.6	760.5	213.5	....	370.0	4636.0	2015.6	67.7	7.3
4	75.5	2747.9	139.8	1281.8	253.0	6.2	321.0	4001.4	2459.7	40.9	7.1
5	80.4	3697.4	159.0	1160.5	327.5	9.4	352.0	5350.9	2988.8	45.6	7.0
6	160.1	3146.3	119.6	319.6	144.0	7.8	321.0	4065.9	1607.8	64.8	7.6
7	127.5	3398.2	119.6	603.1	182.6	15.1	272.0	4673.8	1935.3	40.9	7.4
8	308.4	3647.0	379.6	159.0	132.9	7.8	321.0	4550.9	1206.2	45.6	7.8
9	122.8	3697.4	69.2	530.6	177.9	7.8	321.0	4944.6	1889.6	37.7	7.6
11	453.5	3295.9	1199.9	190.5	151.0	58.2	352.0	3899.0	649.5	68.0	8.3

*No carbonates were present except in No. 11, which had some traces.
†Note extremely high sulfur content of control.

TABLE 8

Analyses of second leachings from pots after 108 days incubation: first series*

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THORUGH	PARTS PER MILLION IN DRY SOIL										
		C as CO₂	C as HCO₃	Cl	SiO₂	Ca	Mg	P as phosphates	K	Na	S as sulfates	Reaction
	cc.											*pH*
1	80	2.1	42.5	814.1	29.2	8.2	10.2	3.36	26.6	363.7	57.8	8.8
2	165	0.0	15.7	979.4	15.1	105.0	30.0	2.33	66.4	763.7	366.9	7.4
3	190	0.0	12.3	413.5	26.4	133.8	32.5	2.33	39.6	442.5	275.2	7.6
4	270	0.0	10.5	873.9	24.5	251.0	66.4	3.35	59.8	598.4	570.0	7.4
5	275	0.0	8.5	212.5	20.7	200.7	44.4	2.34	48.3	371.6	423.6	7.4
6	186	0.0	34.3	1133.8	11.3	48.1	27.4	1.76	93.8	599.9	182.6	8.0
7	160	0.0	32.5	330.6	18.8	26.4	15.5	2.33	37.0	418.8	177.9	8.0
8	287	1.8	45.3	1215.6	7.5	236.6	17.6	2.92	102.0	730.6	114.9	8.8
9	156	0.0	17.3	779.4	4.7	46.9	14.8	1.90	75.9	470.8	192.1	7.6
11		1.6	58.2	708.6	137.0	15.1	19.3	3.77	60.7	377.9	60.0	8.8

*First leaching was made after 14 days incubation.

give the analyses of the leachings and extracts on the first series of experiments of alkali soils.

The data in these tables consist of two classes: one on the leachings, the other on the extracts.   The first class gives the data on the actual amounts

of salts capable of being leached out. The second class presents the data on the changes which took place in the soils on account of the treatment. The extracts were prepared at the same time that the leaching operations were carried out. While not strictly comparable, because of the different conditions in the small flower pots and the large earthenware pots, the data

TABLE 9

*Analyses of leachings from pots after 140 days incubation: first series**

LABORA-TORY NUMBER OF TREAT-MENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL								
		C as CO₂	C as HCO₂	Cl	SiO₂	Ca	K	Na	S as sulfates	Reac-tion
	cc.									pH
1	20	21.8	37.4	2759	1.57	6.2	77.1	1359.0	286.6	8.8
2	210	0.0	35.5	4063	15.1	227.3	333.8	2496.0	796.8	7.2
3	205	0.0	27.5	2669	15.1	141.0	166.9	1762.0	837.7	7.3
4	195	0.0	11.1	2231	16.0	195.1	155.7	1294.0	568.4	7.5
5	205	0.0	26.4	3270	18.8	174.1	190.5	2137.0	1008.0	8.0
6	110	0.0	24.0	2947	6.6	101.5	182.3	1795.0	585.8	7.7
7	205	0.0	38.7	2787	22.6	138.2	151.8	1629.8	626.7	7.6
8	145	0.94	28.6	2137	3.8	28.3	296.2	925.9	154.3	8.2
9	65	0.94	14.1	1677	.....	62.2	85.9	900.7	308.6	8.2
11	10	10.8	14.1	1315	5.5	11.8	92.4	568.4	77.1	8.4

*Some of the pots apparently absorbed some of the salts as indicated by the crust-like formation on the outside.

TABLE 10

Analyses of alkali soil extracts after 140 days incubation: first series

LABORATORY NUMBER OF TREATMENT	PARTS PER MILLION IN DRY SOIL				
	C as CO₂	C as HCO₂	Cl	Ca	S as sulfates
1	1.96	439.6	3050	340.8	601.7
2	0.0	58.0	2700	1443.6	1717.4
3	0.0	64.9	2700	1283.2	1695.6
4	0.0	32.5	2900	1984.9	2187.8
5	0.0	39.3	2400	1644.1	2133.1
6	0.0	131.8	2600	862.1	1312.7
7	0.0	118.0	2650	721.8	1285.3
8	Trace	283.2	2900	280.7	820.4
9	0.0	128.8	2800	501.2	1586.2
11	5.88	383.5	2850	340.85	574.3

on the leachings and extracts from the same incubation periods help to reveal the conditions existing and changes produced in the soil because of the treatments.

We shall take up the fate of the various elements and compounds in the extracts as they are influenced by the treatments.

CHANGES PRODUCED IN THE VARIOUSLY TREATED SOILS AS REVEALED BY
THE EXTRACTS AND LEACHINGS OF THE FIRST SERIES OF EXPERIMENTS

Reaction

After 14 days of incubation the oxidation of sulfur had proceeded far enough to increase the hydrogen-ion concentration of the extracts very markedly. The alum, because of its acid character, also increased the hydrogen-ion concentration of the extract; its power in this respect being equal to that of 2000 pounds of sulfur. After 60 days the reaction shift was still more noticeable in the soils treated with sulfur. Even the 2000-pound application (table 5, no. 6) shows a pH reading of 7.7 against pH 8.8 in the untreated culture. On the other hand it is worth while to note that the alum-treated culture (no. 8) has a pH reading of 8.6, very close to that of the control. Apparently the buffers present in the soil have overcome the little acid present in the alum. The possible reactions of the alum with reference to increase or decrease in hydrogen-ion concentration were discussed in the previous paper (5, p. 401, also 6, p. 26). After 95 days of incubation a general shift of the reaction towards the acid side was apparent. Even the control came to a point where only traces of carbonates could be detected. The reason for that shift could be explained only on the basis of displaced equilibrium. Again the alum treatment without the sulfur showed practically no effect on the reaction at this period of incubation. It is worth while to mention the beneficial effects of the combined alum and sulfur treatments up to a certain point in the incubation periods (no. 9) and the gradual disappearing of these effects upon further incubation. It corroborates the data on the physical effects (5, p. 402); the same explanation may be offered in this connection.

Turning our attention to the data on the leachings it will be noted that the tendency of the reaction confirms the data on the extracts.
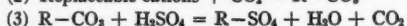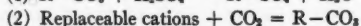
Another point worth mentioning is the effect of the peat on the reaction. The changes produced do not warrant any definite conclusions. There is a tendency towards less alkalinity; it may be due to the utilization of the Na_2CO_3 in the peptization of the organic matter.

Carbonates and bicarbonates

It has already been pointed out that the carbonates and bicarbonates in the untreated cultures are not a constant value, the velocity of the reactions changing from left to right and vice versa. For this reason we find the amount of carbonates and bicarbonates shifting from time to time. On the other hand, the treated cultures showed a progressive disappearance of the carbonates and bicarbonates. After 14 days of incubation the 6000-pound sulfur treatment (no. 4 and 5) showed no trace of carbonates; over 60 per cent of the bicarbonates also disappeared. In the case of the sulfur treatment the sulfuric acid formed, which is the driving force of the reaction, prevents reversion. One of the end products is carbonic acid which upon

decomposition may unite with the cations of the zeolitic portion of the soil and form carbonates again; however, in the presence of sulfuric acid the newly formed carbonates disappear again. The reactions may be expressed in the following equations:

(1) $R-CO_3 + H_2SO_4 = R-SO_4 + H_2O + CO_2$
(2) Replaceable cations $+ CO_2 = R-CO_3$
(3) $R-CO_3 + H_2SO_4 = R-SO_4 + H_2O + CO_2$

After 60 days, even with the 2000-pound application of sulfur, no traces of carbonates could be found and about 40 per cent of the bicarbonates disappeared. In general the rate of disappearance of the carbonates and bicarbonates is increased with the increase of sulfur. Unquestionably the physical improvement of the soils is largely due to the disappearance of the carbonates which peptize the colloids and thus bring into play all the objectionable features of colloids in alkali soils.

The influence of alum treatment on the alkali soil carbonates and bicarbonates illustrates again the contention that its effects are marked in the beginning, but gradually disappear. It will be noticed that after 140 days with the alum treatment (no. 8) only 30 per cent of the bicarbonates disappeared. The combined alum and sulfur treatment (no. 9) is not better than the sulfur alone. It will be recalled that from the standpoint of colloid coagulation the combined effect was greater in some cases than the arithmetic sum of either treatment. The peat treatment did not demonstrate any very marked changes in the combating of the carbonates or bicarbonates. Some decrease in the bicarbonates was the general tendency. As mentioned before the solvent power of the Na_2CO_3 on the peat apparently decreased the amount of bicarbonate. Another feature which should not escape our attention is the variation in adsorption of the various cations and anions at the different incubation periods. The variability of the total carbon as carbonates and bicarbonates at the various incubation periods may be explained on the basis of stronger adsorption at these various periods. The variations are not only true with the carbonates but also with the other cations and anions as shown in the tables.

The data on the leachings show that the bulk of the carbonates and bicarbonates in the alkali soils are retained. Only 20 to 30 per cent of the carbonates and bicarbonates are washed out by leaching. Of course in this first series the flower pot cultures used for leaching and the large earthenware pots used for extracts are not strictly comparable. As pointed out the flower pots absorbed some of the salts since the paraffin treatment did not fully prevent this.

Chlorides

The data on the chlorides in the extracts show that even chlorine, one of the most easily extractable anions, does not always behave in the same way. After 14 days we find that in some treatments the chlorides were held back.

A very strange phenomenon may be noticed after the 60-day incubation period (table 5). Only two-thirds or less of the total chlorides present were extracted. It is possible that the sampling was at fault.[2] The data on the 90 and 145 days' incubation show no sharp variations. The discrepancies may be explained on the basis of increased or decreased negative adsorption. Some of the variations may easily be ascribed to the deterioration of the paraffin coating of the pot, which facilitated absorption by the porous clay walls. In general the treatments have little influence on the behavior of the chlorides in the soil.

The data on the leachings (tables 2, 4, 6, 9) show that the chlorides lend themselves to such treatment, e.g., they are not strongly adsorbed and may easily be leached out. Even the control cultures with a relatively low leaching capacity gave up about the same amount of chlorides as the treated cultures. With only 20 cc. of leachings the control culture after 140 days (table 9) shows the same amount of chlorides as some of the treated cultures which leached through ten times the amount.

The peat treatment showed no influence whatsoever on the course of the chlorides either in the extracts or in the leachings.

Silica (SiO₂)

It has been pointed out (5) that one of the chief colloids present in alkali soils is the silica. In the course of the work a number of difficulties have arisen in connection with the attempts to determine the SiO_2 in the extracts. The chief trouble was due to the failure of the methods to give constant results. At times the extracts had more suspended colloidal material, at times less, although the same methods were used. Of course soil colloids do behave in that way, but still many of the inconsistencies must be credited to the imperfection of the methods.

On examining the data on the SiO_2 it will be noticed that large amounts appear in the extracts from the control culture. The sulfur-treated cultures show only small amounts of silica in solution. The decrease is undoubtedly due to the coagulation of the silica colloids. The alum-treated cultures with or without sulfur accomplished just as good results as the sulfur treatments. It is very probable that part of the aluminum united with the silica forming the insoluble aluminum silicates. Again we must record the very insignificant rôle of peat in coagulating or adsorbing the silica colloids.

The leachings show that the SiO_2 is tenaciously held by the untreated soils, only very small amounts being leached out. We must keep in mind the fact that the untreated cultures did not permit efficient leaching; even in the treated cultures the per cent of SiO_2 leached out is comparatively small.

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[2] The sampling of alkali soils is quite a problem due to the accumulation of the salts at the surface. Generally the samplings were made by boring in several places with a brass tube. This method was found to be satisfactory when done before any salt crust could be seen on the surface.

The inconsistencies apparent from some data in the tables are due to the imperfection of the methods; the general tendency, however, is as outlined above.

Calcium

Even the water extracts of the control cultures contain some calcium. Although the extractions were made uniformly in the same manner, still the amount of calcium extracted was different at every extraction. The reason for this phenomenon may be found in the well known equilibrium displacement, which may occur in the system alkali soil—soil solution. The compounds which calcium forms in the alkali soil solution are, of course, problematic. From the nature of chemical reactions we should expect the calcium to precipitate. From solubility studies, we know that the most probable insoluble compound under the conditions would be $CaCO_3$. In 100 cc. of water only 0.00052 gm. of Ca as $CaCO_3$ may be found at room temperature while actually after 60 days the control cultures showed 0.00479 gm. of Ca in 100 cc. of extract. There was over nine times as much Ca in solution as could be if all had been in the carbonate form. Bicarbonate is of course not excluded; it is, however, more logical to assume the presence of gypsum, since the soil solution contains an abundance of sulfates; it is very likely that the sulfate and carbonate are found in a condition of displaced equilibrium with the sulfate in the lead. In 100 cc. of solution it is possible to have 0.0529 gm. of Ca as gypsum or about ten times as much as was actually found. However, in such analyses we must keep in mind the soil solution with its reaction power due to the presence of various salts on one hand and the small concentration of the solvent on the other. The soil solution of the alkali soils is rich in chlorides and it is possible that some calcium exists in alkali soil solution as chlorides. The oxidation of sulfur brings into solution more calcium; the amount increasing with the increase of sulfur application. The question arises: where does the calcium come from? That it is not present in the form of carbonates that became soluble with the oxidation of the sulfur may be deduced from the pH readings, also from the data on the magnesium, a discussion of which is to follow. The total carbonates present are not sufficient to take care of the calcium as carbonates. The explanation must be sought in the replacement process in the zeolitic portion of the soil due to the high coefficient of absorption of the hydrogen from the sulfuric acid.

With the advance of the period of incubation the ratio of calcium brought into solution to sulfur oxidized is narrowing. For the first 60 days the ratio of calcium to sulfur was about 1 to 5; after 95 days the ratio was about 1 to 2 and after 140 days it was 1 to 1 and even lower in the cultures with large amounts of sulfur. The narrowing of the ratio of calcium to sulfur indicates that with the increased period of incubation the efficiency of the hydrogen ions from the sulfuric acid as a replacing agent is increased. The

explanation is fairly simple; in the first period of incubation there are in the soil solution a number of compounds capable of reacting and, of course, these are first to be attacked by the sulfuric acid. When the compounds in solution [in our case the soluble carbonates and colloids mentioned (5)] have been acted upon, the hydrogen ions are free to react with the zeolitic portion of the soil which then plays its part in the replacement process. As a result we get more calcium replaced in the later periods. These reactions have to be considered in any of the quantitative studies of cation replacement, such as the Gedroiz method (2). It is strange that this careful investigator left out these reactions in his studies. It is very likely that at this point all of the zeolitic calcium was replaced. The question naturally arises whether such a course is desirable in this particular alkali soil? The replacement of the calcium with hydrogen brings about, what Gedroiz calls, an unsaturated condition, it forms a hydrous aluminum silicate; this condition theoretically forces the alkali soil to an acid condition. It is a question which is very closely connected with the possible influences of the composition of the irrigation waters and the salts coming up from the lower horizons. From the data on the sodium content of these soils it seems that such salts come from below to the surface horizon. Even though the sodium has not a high coefficient of adsorption, when present in large amounts it will eventually replace the hydrogen ions and form a sodium alkali soil, especially after all the sulfur has been oxidized. However, under the conditions existing in the soil solution with appreciable amounts of calcium, it is very likely that the calcium after having been first replaced by the hydrogen will get back first into the zeolitic portion and the sodium may be washed down again, since the soil will be permeable to water. When left alone at this stage the alkali will come back, since an accumulation of sodium salts will produce again a sodium saturated zeolite, but if the alkali soil colloids may be kept down by small applications of sulfur, the washing out of the sodium salts will keep the soil in good condition. Of course this mode of treatment is problematic and if applicable it is adapted only to this particular soil under investigation. The knowledge of the replaceable cations in the zeolitic portion is of prime importance.

The condition of the alkali soils under investigation as revealed by the calcium and other data may be summed up from the standpoint of the theories advanced by Gedroiz as follows: The presence of the calcium as the chloride is not desirable and the washing out together with the sodium salts brings about a favorable condition for the formation of calcium carbonate and sulfate in the soil; this comes about with the further replacement of the calcium and sodium from the zeolitic portion. When left alone the calcium, which has a higher coefficient of adsorption than the sodium, will tend to enter the zeolite again. This will be possible after the driving force of the reaction, the hydrogen ions of the sulfuric acid, cease to be in excess.

The presence of larger amounts of calcium in solution is beneficial from another standpoint. The calcium, as pointed out by the studies of Loeb (7) and Osterhout (8) counteracts other injurious influences; in this case the soluble sodium salts. After washing out the soluble salts, an addition of lime—preferably burned lime—will increase the driving force of the calcium ion and the zeolites will get back the calcium. At this stage the colloids will be coagulated through the combined action of the hydrogen which is to come from the unsaturated zeolite and the soluble calcium in solution. This will, as pointed out, facilitate the leaching out of the undesirable sodium salts, which have the tendency to increase the colloidal fraction of the soil.

When we examine the leaching data we find that on the average not more than about 15 per cent of the calcium was leached out. This is very significant: the rôle this calcium is to play in the soil solution, after the alkalinity has been destroyed and the soluble salts washed out, is very important, as pointed out above.

A glance at the analyses of the extracts and leachings show that the alum has no power of replacing the calcium: the alum extracts do not show more calcium than the control cultures. There is, however, the possibility that on account of the low hydrogen-ion concentration of the alum-treated cultures, the replaced calcium formed calcium carbonate and exists as such. The importance of the reaction in the replacement process has not been studied. Even Gedroiz overlooked this extremely important factor.

In table 8 we find the data on the second leachings; the figures on the calcium from these leachings show that there was practically the same amount of calcium as in cultures which have been leached for the first time at about the same period of incubation. This would seem to indicate that the calcium as shown in the data on the extract does not represent the calcium in the soil solution; it is rather the calcium soluble in the amount of water used for extraction. The leachings do not give the true value for the calcium in the soil solution; they only show the amount of calcium capable of being dissolved in the amount of water used in the leaching operations. This may be inferred from a comparison of the calcium leached out the first time (table 2) and that leached out the second time (table 8). If we only remember the leaching capacity of the cultures at the two different periods as judged from the number of cubic centimeters leached through, we can easily see that the amount of calcium is about the same in both instances. The dynamic nature of the system (soil plus soil solution) and solubility studies predict such behavior. This phenomenon has a bearing on the practice of leaching in the field. It would seem that one leaching would be sufficient, since the calcium continues to come out from the zeolites and since the sulfur continues to oxidize even without leaching. There is, therefore, no necessity of further leaching and thus wasting plant-food. Greaves, Hirst and Lund (3) point out among other things that the phenomenon of non-productivity noticed on alkali soils after leaching may be partially due to the lack of phos-

phorus.   There may be other factors, however, which would favor a leaching at an early period first and another one at a later period.

The unusually high calcium content in the second leaching of the alum-treated culture (no. 8) is very peculiar.   It is the only case where the alum shows such a high replacement power.   It may be argued that after leaching the calcium had a better chance to come out from the zeolitic portion.   It seems as if the presence of the alum prevented the replacement of the calcium.   This, however, has still to be proved.

Magnesium

A critical examination of the magnesium in the extracts seems to show that this particular soil has not much if any replaceable magnesium in the zeolitic portion.   In other words this alkali soil is not a magnesium alkali soil, following the nomenclature of Gedroiz.   The slight increases of the magnesium content in the extracts are insignificant as compared with the calcium increases as the period of incubation is advanced.   The leachings show that only very little of the magnesium is washed out.   The fact that the magnesium content does not increase even in the cultures with the highest amount of sulfur seems to show that it does not exist as the carbonate. It also suggests the same condition for the calcium.

Phosphorus

The data on the phosphorus do not throw much light on the subject.   The oxidation of the sulfur seems to put the phosphates into an insoluble state. Apparently, the organic material as it is dissolved by the soda, carried much organic phosphorus.   As the colloids are coagulated and the peptization of the organic matter by the soda ceases, the phosphorus content is decreased. The alum does not show any variations in the phosphorus content, except in the first period of incubation (14 days).   The coagulation effect of the alum at this time is responsible for the diminution of the phosphorus in solution. It could not be the interaction of the aluminum with the phosphates, since the latter exist in organic form.

Sodium

We are to consider the element which is generally looked upon as the chief injurious agent in alkali soils.   It has been shown already that according to the most recent knowledge on the subject of alkali soil formation the origin of such soils is to be sought for in the replaceable cations of the alumino-silicate complex known as zeolites.   The salinizing process which may take place in one or more horizons of the soil profile for one or more reasons saturates the zeolites with some cation and this cation determines the nature of the alkali soil.   It may also happen that two cations are responsible for the process.   This salinizing process is followed by a desalinizing period at and

after which the soda appears; the appearance of the soda indicates that some sodium may be present in the zeolitic portion. As stated above this does not exclude any other cation. From the data on the calcium it was concluded that the soil under investigation was saturated with calcium in the zeolitic portion; thus the soil is undoubtedly partially a calcium alkali soil.

The data on the sodium from the extracts of the first series are available for one period of incubation only; still the reactions may be well inferred: there is an increase in the sodium content of the extract amounting to 50 per cent in the 6000-pound sulfur application. It is a great deal less in the other treatments. We can safely infer, however, that there is an increase in the sodium content with the advancement of the incubation period. Therefore, it seems that at least in its make-up the soil under investigation is not a purely sodium alkali soil. The presence of the large amounts of soluble sodium may be due to the fact that this soil is in process of desalinizing accompanied by the formation of soda, or more likely just the reverse may be true, i.e., the sodium is just beginning to invade the soil.

The data on the leachings show that sodium is leached out in appreciable amounts. Fifty per cent or more of the sodium is leached out with the first leaching operation. The figures in the first series are not so reliable since the walls of the clay pots have undoubtedly absorbed considerable of the soluble compounds.

Potassium

The potassium as revealed in the data is not of any great moment in the alkalinity of the soil investigated. The oxidation of sulfur does not increase the amount of potassium in the extract; apparently there is no zeolitic potassium to be replaced. The leachings show that potassium is not held back in this soil.

Sulfur

The initial high concentration of sulfates did not prevent the oxidation of the added sulfur. This may be judged from the data on the sulfates in the extracts. The rate of oxidation has been given in a previous paper (6) and need not be repeated here. In general it will be noticed, that with the higher applications of sulfur the advantages gained by the exchange of cations in the zeolitic portion are greater, e.g., more of the replaceable cations are forced out. As already mentioned it is the hydrogen ion of the sulfuric acid formed that is responsible for the replacement, having a high coefficient of adsorption. As the sulfates increase, the chances for the formation of gypsum and sodium sulfates (provided our supposition of the calcium-sodium alkali soil is correct) rather than calcium carbonate and sodium carbonate, are also increased. In any alkali soil the advantage of the presence of sulfuric acid consists in the combination of the sulfate radical with the replaced cations, preventing the formation of carbonates. The reactions involved

were given in the section on the carbonates and bicarbonates. Mention should be made of the reactions taking place in solution before replacement takes place. As pointed out (see p. 140) the replacement brings out cations which may combine with the CO_2 from the decomposition of the original carbonates present and other sources such as soil, air and decomposition products of the soil microbial flora. The distinct advantage of the sulfur as compared with gypsum lies in the formation of carbonic acid which is easily broken down as may be seen from the equation (see p. 140). When all of the replaceable cations are out from the zeolitic portion we should have an unsaturated soil, i.e., one which has replaced in the alumino-silicate complex all the replaceable cations by hydrogen.[3] Such a soil should be a true acid soil, but it is questionable whether it would be desirable to bring about such a condition. From the data on the second leachings (table 8, no. 6 and 7) we are justified in assuming that the 1-ton application of sulfur is not sufficient to replace all the cations in the zeolitic portion. The reaction of these leachings shifted back towards alkalinity, indicating that after the excess of the soluble sodium salts has been washed out by the first leaching more of the replaceable cations left the zeolitic portion, to form carbonates. Since all the sulfur has apparently been oxidized there was no more sulfuric acid to react with the carbonates. The reduction of the amount of soluble sulfates allows the formation of the carbonates.

A clearer understanding of this phenomenon will be brought out when we analyze the data on the second series.

The data on the leachings are significant inasmuch as they show that as soon as the colloids are coagulated and leaching operations are facilitated 50 or more per cent of the sulfates are leached out.

Nitrogen

The soil under investigation is poor in nitrogen, the total content being 0.0479 per cent. It is rich in nitrates and the soluble nitrogen is thus fairly high, amounting to about 25 per cent of the total. The action of the sulfur is to decrease the amount of soluble nitrogen in the extract. The decrease is undoubtedly due to the coagulation of the organic colloids which are rich in nitrogen. The leachings seem to carry much of the soluble nitrogen and

[3] The theory of base exchange as outlined for the zeolites through the replacement of their cations by the hydrogen-ions of the sulfuric acid *presents a new aspect of soil acidity*. We may picture it as follows: a soil becomes acid when its zeolitic portion (the portion capable of exchange) is saturated with hydrogen, and there are no more basic substances to be replaced and come out in solution. Only then will free acids (mineral or organic) or acid salts appear in the soil solution. Uutil then no real acidity, i. e. free acids, is possible. The zeolites partially saturated with hydrogen may show acidity when treated with neutral salts. In this case the replacement process described in this paper takes place; in other words, the cation of the neutral salt replaces the hydrogen. These considerations have been suggested in the course of the alkali soil investigation and are now being looked into.

the losses should be taken care of when the soil is ready for cropping. The best forms of nitrogen to apply would be the organic forms and ammonium sulfate. Experimentation in this direction will determine the best method of procedure.

Peat

In analyzing the behavior of the various cations and anions in the differently treated alkali soils, mention was made of the influence of peat in alkali soil treatment. The peat did not have any striking effects. In general it would be expected that the humates and the cations combined with them would react with the cations present in solution and thereby have an effect on the replacement process in the zeolitic portion and also on the general shift of the cations. It is known that the cations in the humates are in loose combination. Examining the tables on the extracts and leachings one may note that up to the higher periods of incubation the calcium is greater in the cultures treated with peat in combination with sulfur. The reverse is true with the alum treatment and peat, or the peat alone. The authors suggest the possibility of replacement of calcium in the humates by hydrogen from the sulfuric acid augmenting the total amount of calcium.

Gedroiz (1) stresses the point of similarity between the cations of the zeolites and the humates, and the facts on hand are in accord with the theory. As the period of incubation advances there is apparently no more calcium to replace. On the other hand, alum treatment with peat and the peat alone apparently caused none of the calcium to be replaced. If the course of reaction with the peat as outlined is true, then there is some advantage in adding the peat. Moreover, the peat serves as a buffer taking up some soda, reducing temporarily the alkalinity. This may be noticed from the data on the carbonates.

SUMMARY

In summing up the result of the first series of experiments this may be said: the 2000-pound sulfur treatment is not sufficient to bring about a complete transformation of the alkali soils. The sum total of hydrogen ions from 2000 pounds of sulfur available for replacement of the zeolitic cations and neutralization of the existing and potential soda is not sufficient. The alum has some merit, especially in combination with sulfur. This point will be discussed more fully when the second series of experiments is taken up.

The evidence on hand seems to point to the calcium-sodium character of the particular alkali soil under investigation. The soil is probably in process of desalinizing or more likely in process of formation. These postulates are based on the theories advanced by Gedroiz.

In the next and last paper the data on the second series of experiments will be taken up; the results of the effect of the treatments on some of the biological activities will be brought out; and also some vegetation experiments will be reported.

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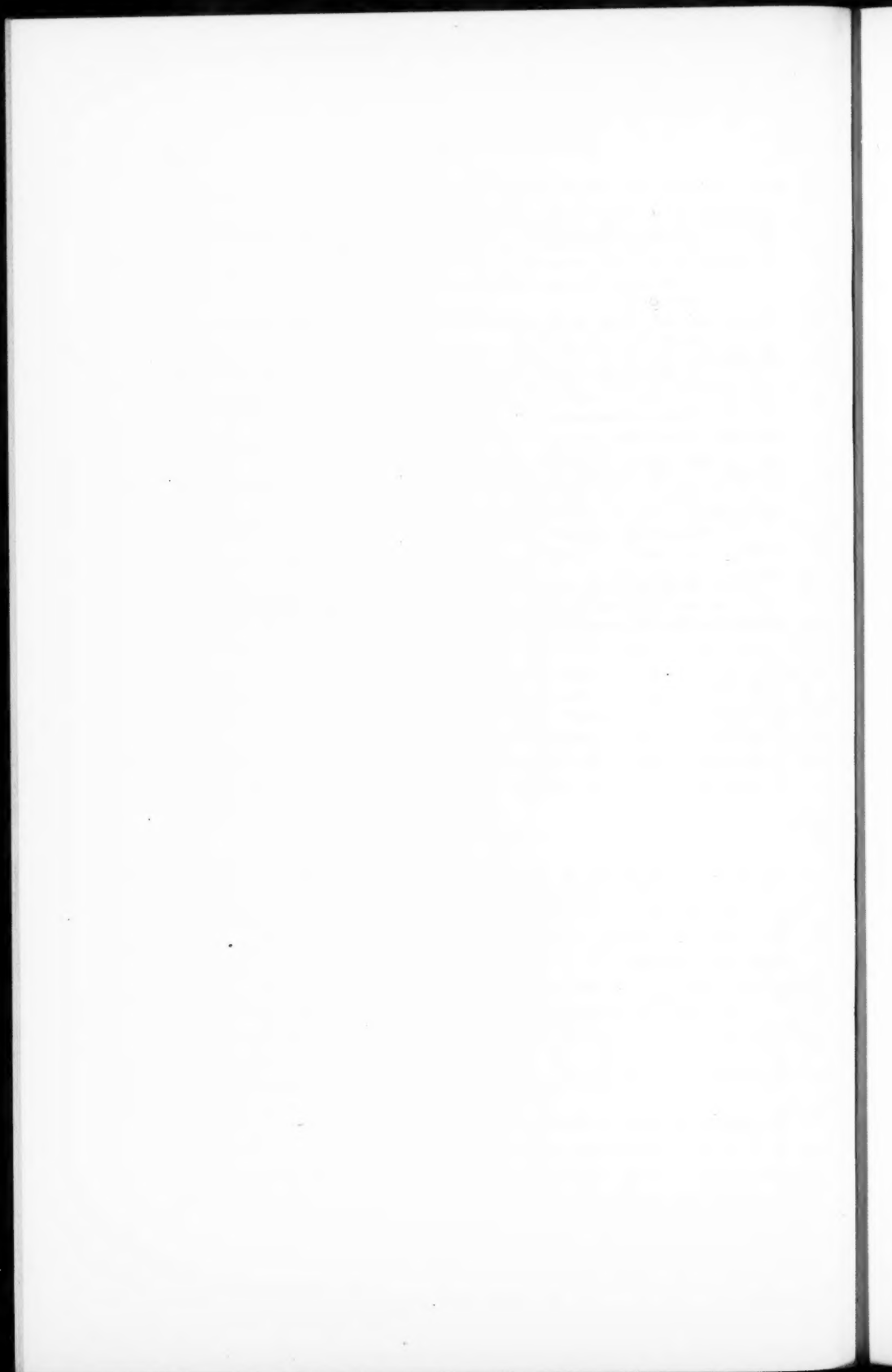
SECULAR AND SEASONAL CHANGES IN THE SOIL SOLUTION

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In a recent paper we have shown that solutions obtained from soils by a process of water displacement have many of the properties which the true soil solution should possess (2). Briefly stated:

a. The freezing-point depressions of such solutions are approximately equal to those obtained by direct determination upon the soils from which they are respectively derived when the soil displaced contains relatively large amounts of water (i.e., amounts optimum for plant growth).

b. Successive increments of solution from a given displacement have equal concentrations of electrolytes up to the point where dilution by the displacing water occurs.

c. There is an inverse relation between the concentrations of total electrolytes and of some of the individual solutes in the solutions obtained and the initial moisture contents of the soil as packed in tubes prior to displacement.

d. Concentrations of solutes in the displaced solutions are the same as those computed from water extractions for those constituents for which water extraction is a valid criterion (i.e., for substances—nitrates and chlorides—which are presumably always completely dissolved in the water of the soil when the latter contains amounts of water adequate for plant growth).

e. Concentrations of solutes in the displaced solutions are generally lower than those computed from water extractions for those constituents for which water extraction presumably gives too high results (i.e., for substances which are presumably present in part in the solid phase).

The above-stated facts and relations leave little doubt that such displaced solutions are substantially identical with the true soil solution of soils containing considerable moisture (conventional optima for plant growth). A difficulty presents itself, however, with respect to soils containing small amounts of water. Thus, while we have found, as stated above, that the freezing-point depression determined directly upon the soil is approximately equal to that of the displaced solution at high moisture contents, a similar agreement is not obtainable in soils at a low degree of moisture. It is therefore evident that either the freezing-point depression or the displaced solution from soils containing small amounts of water is defective as a measure of the soil solution. We have shown, however, that there is an inverse relation between total concentrations of electrolytes in the displaced solutions and the initial moisture contents of the soil. This latter result is what we should expect if all of the water of the soil is effective as a solvent and if no solutes are removed from the

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liquid phase by a decrease in the moisture content of the soil. Other evidence indicates that while there is some removal of solutes from the liquid phase with decreased moisture, such removals are relatively so small as to have little effect in disturbing the inverse relation of total concentration and moisture content. This relation and the agreement in freezing-point depression of displaced solution and soil at high degrees of moisture suggests an equivalence of the displaced solution and the true soil solution at body high and low moisture contents. The discrepancy between the freezing-point depression of the soil at low moisture contents and that of the displaced solution, deprives us of the evidence which would tend to make conclusive the proof of an absolute identity of displaced solution, and soil solution but does not negative such a conclusion. Rather do the facts suggest that the discrepancy is due to the inadequacy of the freezing-point depression made directly on the soil at low moisture contents as a measure of the concentration of the soil solution.[1]

Much other evidence, based upon careful studies of the qualitative and quantitative composition of displaced solutions and water extracts, tends to confirm our general conclusion. A theoretical difficulty presents itself in that it is impossible to conceive of such a thing as a physical partition between liquid and solid phase without disturbing the equilibrium as it exists in the soil. Even so, it by no means follows that changes in the liquid phase during the process of displacement are of substantial magnitude. In the light of all of the facts, the writers are of the opinion that the differences in total concentration and composition of electrolytes in the true soil solution from those of displaced solutions which satisfy certain criteria we have set up (2), are so small as to be without significance in terms of the capacity of the soil to produce crops.

Assuming the adequacy of the displaced solution as a measure of the true soil solution, it is evident that we have at our disposal a more accurate means of ascertaining the condition of the soil and the effect of environmental conditions upon its soluble matter, than has hitherto been available. The opportunity is thus presented of confirming in a definitive manner the conclusions based upon the results of water extractions (6) and of extending our knowledge by the measurement of those changes in the soil which are otherwise imperceptible. If our assumption is correct, it should, for example, be an easy matter to confirm substantial variations in the displaced solutions obtained from cropped soils at the beginning and end of a period of years and even of a single season, thus measuring the effect of crop withdrawals and other factors upon the soil solution.

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[1] The discontinuous character of the soil film in soils of low moisture content has, for some time, appeared to the writers as the indirect cause of freezing-point aberrations in such soils. Recently, through the courtesy of D. R. Hoagland, we have learned of certain verbal suggestions of E. A. Fischer which appeal to us as affording a reasonable explanation of such aberrations.

Since the importance of the displaced solution has only recently become recognized, it is obvious that sufficient time has not elapsed to permit of the accumulation of the evidence as to changes in displaced solutions obtained from a single mass of soil over a period of years. We happen, however, to have at hand a number of different soils collected in 1915, each of which was, at that time, made physically homogeneous by sieving and mixing, and then divided into three large (1800-pound) portions. Each of these portions has been continuously maintained under different conditions of treatment for 8 years.

One portion of each soil has borne a crop of barley every season; one portion bore a crop the first year (1915), but has lain fallow during all succeeding years; and the third portion has been kept in the air-dry condition and stored in tightly covered bins for the entire period. The justification for presenting this paper and for its title is the belief that the air-dried portions of soil have remained practically unchanged and that the data recently obtained from solutions displaced from such portions represent the condition of the soils from which they were respectively derived at the time they were first assembled.

If this is true, it is evident that we may legitimately compare the data recently obtained by displacement from the various portions of each soil to determine the effect of time and cropping upon its qualitative and quantitative composition. For convenience, we shall refer to the portions of soil which have been continuously cropped as "Cropped Soils (A)": to those which were cropped in 1915, but which have subsequently lain fallow as "Fallowed Soils (B)"; and for the portions kept in closed bins as "Air-Dry Stored Soils (S)."

All soils were sampled and displaced, and the displaced solutions analyzed in the spring of 1923. At the time of sampling both the fallowed and stored sets of soil were very dry and it was of course necessary to add water and permit the soils to come into equilibrium therewith before conducting the displacements. The cropped soils (A) had had the maximum opportunity to recuperate from the effects of crop withdrawals during the preceding season. The differences observed in the displaced solutions of these soils from those of their fallowed and air-dry duplicates, may reasonably be ascribed to the treatment (i.e., cropping) for the entire 8 years and not to seasonal variation. The effects of seasonal variation are shown by other data presented hereinafter.

The data for the 8-year period are given in table 1.

It will be observed that the moisture contents of the fallowed and stored portions are fairly uniform for each soil, but that the cropped portions were for the most part displaced at considerably lower moisture contents. Since the concentration of displaced solutions varies with the initial moisture content of the soil, only the most general comparisons can be made from the original data without allowance for the effects of the different moisture contents of the cropped soils. Such a calculation to uniform moisture content involves the assumption that the concentrations of each constituent are in an exact inverse proportion to the moisture contents of the soil, which is not strictly

true. Hence it is desirable to bring out a few facts from the original data before making the conversions necessary to the further discussion. The limitations of the calculations to uniform moisture content will be discussed in their proper place.

TABLE 1

Displaced solutions from cropped (A), fallowed (B), and air-dry stored (S) soils after 8 years

SOIL	MOISTURE	pH	PARTS PER MILLION OF DISPLACED SOLUTIONS										
			NO₃	HCO₃	Cl	SO₄	PO₄	SiO₃	Ca	Mg	Na	K	Total*
	per cent												
7A	10.7	7.4	174	83	0	655	1.1	—	283	106	49	24	1375
7B	16.8	7.6	1696	73	52	432	1.2	—	640	128	71	36	3129
7S	16.0	7.2	1468	69	313	184	3.3	38	547	112	123	39	2896
8A	9.6	7.4	274	93	0	633	2.5	—	267	93	31	20	1414
8B	15.1	7.0	1746	59	40	432	4.0	—	573	155	66	75	3150
8S	14.7	6.9	2182	77	260	451	7.2	61	539	204	156	156	4093
9A	11.4	7.6	160	73	0	432	0.9	—	213	75	27	12	993
9B	15.4	7.6	947	63	36	420	1.2	—	460	93	53	29	2102
9S	15.1	7.3	680	46	372	184	2.9	33	380	75	88	21	1882
10A	13.9	7.2	230	40	0	360	1.2	—	187	145	23	33	1019
10B	18.0	7.0	1704	34	32	348	2.1	—	547	136	·47	74	2924
10S	18.5	6.8	937	34	348	148	4.0	51	360	91	115	89	2173
11A	12.9	8.2	166	160	0	645	3.3	—	213	93	84	39	1403
11B†													
11S	15.5	7.8	1049	171	367	344	12.1	49	407	128	203	100	2830
12A	12.1	7.3	115	40	0	281	2.3	—	120	46	27	13	644
12B	14.8	7.0	1503	34	40	337	0.3	—	585	151	60	45	2755
12S	15.1	7.3	208	39	80	170	3.1	48	145	48	52	30	823
14A	18.0	8.0	146	107	0	295	1.3	—	140	47	56	45	837
14B	17.9	7.4	1766	54	60	397	1.7	—	547	139	85	118	3168
14S	18.5	7.4	779	78	100	188	4.3	54	290	91	74	89	1747

* Sum of determined solutes.
† Soil not available for study.

The reader will observe from an inspection of table 1 the more obvious effects due to the different conditions under which the soils have been maintained and to the effects of cropping. Briefly, the concentrations of total electrolytes, of nitrates, and of several of the individual ions are, for the most part, materially decreased by cropping for a series of years, and increased by fallowing. Soil 8 constitutes an exception in that fallowing apparently has caused a decrease in concentration. This soil, however, has the highest con-

centration of any which we have studied, and the changes observed therein probably represent a type of effect characteristic of soils in a high state of fertility, in that stimulation of biological activities due to the treatment may result in diminished concentrations. Such an effect is consistent with field results with soils which do not respond to fallowing by increased production. Indeed, the stimulation of biological activities induced by too intensive, mechanical treatment in the processes of plowing, harrowing, and cultivation, are well known to be unfavorable to many sandy soils in the arid region. This result is variously ascribed to oxidation of organic matter, loss of nitrogen, and decrease in moisture-holding power, but it may also be in part caused by, or attended by, diminished concentrations of certain constituents of the soil solution.

CALCULATION TO UNIFORM MOISTURE

Since our previous studies of several of the soils used in the present work show that the concentrations of total electrolytes, nitrates, chlorides, and in these soils calcium, in the displaced solution, appear to vary inversely with the moisture contents of the soils, we may compute the approximate concentrations which would have been present in the displaced solutions from the "A" soils, had these been obtained at the same moisture contents as those of the "B" or "S" soils. However, we have also shown in previous work that this inverse relation does not hold exactly with reference to certain ions. Thus, when the moisture content of the soil is doubled, the concentration of the potassium ion in the displaced solution is somewhat more than half that obtained from the soil at the lower moisture content. In such calculations involving the potassium ion, the figures obtained, therefore, will be somewhat lower than the truth. They will represent minima which approach the truth to the extent to which the inverse relation holds, or, stating it another way, to the extent to which solid-phase potassium enters the solution when the moisture content of the soil is increased. The data of table 2 are of interest in this relation.

Such great percentage variations require that data to which they apply shall be interpreted with caution. It will be shown later (table 3), however, that the potassium-ion concentrations in the fallowed or air-dry soils are in no case less than 100 per cent greater and are frequently two, three, or four times as great as those of the cropped soils. Such differences are clearly due to the treatment of the soil and are not assignable to the inadequacy of the moisture correction.

We have also observed heretofore that the magnesium ion in our soils behaves in general like the potassium ion, so that the figures corrected for moisture will likewise represent minima. No study has yet been made of the sodium ion in this relation, but it is highly probable that any cation may, in part, be removed from solution by the reduction of moisture in the soil. In this case, also, we may, therefore, assume that the corrected figures represent minimum

TABLE 2

Potassium ion in displaced solutions at various moisture contents of soil as determined and as calculated

	SOIL 8		SOIL 9		SOIL 11	
	Moisture		Moisture		Moisture	
	per cent	*p.p.m.*	*per cent*	*p.p.m.*	*per cent*	*p.p.m.*
Determined..............	7.3	250	7.5	130	8.0	165
Calculated..............	14.6	125	15.0	65	16.0	83
Determined..............	14.8	150	14.3	85	16.6	140
Approximate variation..	−17 per cent		−24 per cent		−41 per cent	

TABLE 3

Displaced solutions from cropped (A), fallowed (B), and air-dry stored (S) soils after 8 years
(Results from table 1, calculated to a uniform moisture basis for each soil)

SOIL	MOISTURE	pH	PARTS PER MILLION OF DISPLACED SOLUTIONS										
			NO$_3$	HCO$_3$*	Cl	SO$_4$	PO$_4$*	SiO$_3$	Ca	Mg	Na	K	Total
	per cent												
7A		7.4	116	83	0	438	1.1	—	189	71	33	16	947
7B	16	7.6	1781	73	55	454	1.2	—	672	134	75	38	3281
7S		7.2	1468	69	313	184	3.3	38	547	112	123	39	2896
8A		7.4	179	93	0	413	2.5	—	174	61	20	13	955
8B	14.7	7.0	1798	59	41	445	4.0	—	590	160	68	77	3242
8S		6.9	2182	77	260	451	7.2	61	539	204	156	156	4093
9A		7.6	121	73	0	326	0.9	—	161	57	20	9	750
9B	15.1	7.6	966	63	37	428	1.2	—	469	95	54	30	2144
9S		7.3	680	46	372	184	2.9	33	380	75	88	21	1882
10A		7.2	173	40	0	270	1.2	—	140	109	17	25	775
10B	18.5	7.0	1658	34	31	339	2.1	—	532	132	46	72	2846
10S		6.8	937	34	348	148	4.0	51	360	91	115	89	2173
11A		8.2	138	160	0	537	3.3	—	177	77	70	32	1200
11B†	15.5												
11S		7.8	1049	171	367	344	12.1	49	407	128	203	100	2830
12A		7.3	92	40	0	225	2.3	—	96	37	22	10	524
12B	15.1	7.0	1473	34	39	330	0.3	—	573	148	59	44	2701
12S		7.3	208	39	80	170	3.1	48	145	48	52	30	823
14A		8.0	142	107	0	287	1.3	—	136	46	54	44	817
14B	18.5	7.4	1709	54	58	384	1.7	—	529	135	82	114	3069
14S		7.4	779	78	100	188	4.3	54	290	91	74	89	1747

* Bicarbonate and phosphate remain as in table 1 (see text.)

† Soil not available for study.

values. Preliminary studies of the behavior of the sulfate ion also indicate that a portion of the sulfate in some soils is removed from solution at diminished moisture contents; the computed figures, therefore, also represent minima.

In the case of phosphate, all of the evidence from displaced solutions and water extracts indicates that equilibrium of liquid- and solid-phase phosphate is established very rapidly so that changes in the moisture content of the soil do not appreciably change the phosphate-ion concentration. Thus phosphate concentration is independent of moisture content and no correction is necessary for this ion. The fact that bicarbonate is a weak ion and tends to form relatively insoluble carbonates suggests that its behavior should be more like that of phosphate than of any other ion. We should, therefore, anticipate that increasing the amount of moisture would not greatly decrease the concentration of this ion. A careful study of one of our soils (no. 12) gave 73 and 61 parts per million of the bicarbonate ion in the solution obtained by displacement when the soil contained respectively 7.4 and 15.0 per cent of moisture. The conventional correction for moisture content would, in this case, have given results so far from the truth as seriously to vitiate conclusions drawn from the data. Since the correction is inapplicable, we have merely repeated the original figure for bicarbonate in the corrected tabulation. The figures for bicarbonate in the "A" soils (table 3, see also table 5) therefore represent maxima.

EFFECT OF 8 YEARS' FALLOWING[2] ON DISPLACED SOLUTIONS

(Comparison of results from fallowed "B" with stored "S" soils continuously maintained in the air-dry condition for 8 years)

In five out of six cases, the total electrolytes and nitrates in the displaced solutions are substantially higher in fallowed soils than in the stored soils. In the case of soil 8, an exceptionally productive soil (as shown by crop records from the cropped duplicate for the first two years), there is a falling off in total concentration of displaced solution in the fallowed portion. The one exception, the causes of which are readily accounted for (page 155) does not weaken the conclusion that soils in general tend to have increased concentrations in their displaced solutions, if they are allowed to remain uncropped under conditions somewhat favorable to biological activity (aeration, moisture, etc.). It can hardly be doubted that under such circumstances, there is an increased concentration of the soil solution and that this result is an important cause of increased productiveness when such soils are eventually cropped.

[2] The so-called fallowed soils were actually cropped the first year and cultivated and watered the first 4 years. The remaining 4 years, they received no treatment other than weeding. Strictly speaking, therefore, the soils were not fallowed in the sense in which the word is used in field practice. We have deemed it necessary to use the term as being more nearly descriptive of the treatment as a whole than that supplied by any other abbreviated expression.

When we consider the effect of the treatments upon individual ions, it is obvious that these must, in general, follow the total concentration. Inspection of the results shows that the five soils which have increased total concentrations due to fallowing, have markedly increased in nitrate, sulfate, calcium, and magnesium.

In all cases, where data are available, the chloride ion not only diminishes, but tends, comparatively speaking, to disappear. Since chloride should always be present in the liquid phase, except when very high concentrations are involved, the cause of loss of this ion is not at first obvious. It should be recalled, however, that the "B" soils which we are calling fallowed soils for the period as a whole, were, in fact, cropped for the first year (see footnote, p. 157). The results of numerous investigations in this laboratory and elsewhere testify to the ease with which chloride may be absorbed by plants and thus removed from soils (4). It seems fair to conclude that the one crop grown on the so-called fallow soils has caused the effect observed. It should be noted in this connection that after 8 years' cropping ("A" soils), all chloride had been removed from all soils.

EFFECT OF 8 YEARS' CROPPING ON DISPLACED SOLUTIONS

(Comparison of results from cropped "A" soils, with fallowed "B" soils and with stored "S" soils continuously maintained in the air-dry condition)

The extraordinary falling off in concentration of total solutes and nitrates in the displaced solutions from the cropped soils is at once evident. With one exception (magnesium in soil 10), which we have reason to believe from other data represents an erroneous determination,[3] all of the cations are lower in the displaced solutions from the cropped soils than in those from the stored soils by what appear to be significant and in most cases by very substantial amounts. That such differences reflect and measure with considerable accuracy the changes which have taken place in the soil solution can hardly be doubted. The greatly diminished crops which have been taken from the soils during the latter years of the experiment are consistent with, and in our view, largely caused by these changes.

Two features of the changes due to cropping deserve special comment, viz., the decreases in phosphate concentration and the increases in sulfate. The phosphate results, in so far as we are aware, are unique in that they represent fairly accurate measurements by a rational procedure of changes in the concentrations of this ion in soils. With the exception of phosphate in 12B,

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[3] This discrepancy and the one noted in the following paragraph with reference to phosphate was not discovered until our solutions were exhausted. The first is unimportant for the purpose of our present discussion. The second if literally interpreted involves an unfortunate variation from a general type of behavior. Since phosphate behavior in soil is now undergoing special examination in this laboratory it was not deemed necessary to repeat the work on this soil for present purposes.

which may be erroneous,[4] the results are absolutely consistent, the stored soils having the highest, the fallowed next highest, and the cropped soils the lowest concentration, respectively.

The interesting question arises as to whether the diminished phosphate concentrations in the cropped soils are due to withdrawals by the plant or to some other cause.   As stated repeatedly in the publications of this laboratory and as is obvious from any rationa lconsideration of the chemical properties of phosphates, as well as from the results of the extraction of phosphate from soils by varied proportions of water, it is clear that phosphate tends to form a saturated solution with respect to any particular physico-chemical system. Moreover, if from any cause (such as dilution), the phosphate concentration is changed, equilibrium tends to re-establish itself very rapidly.   These considerations render it difficult to understand why cropping should cause a general decrease in the concentration of phosphate in the soil solution unless the change is accompanied by substantial increases in the concentrations of those cations (particularly calcium and to a lesser extent magnesium) which tend to form relatively insoluble phosphates; or unless the alkalinity of the soil is increased. It will be observed as between the figures from the cropped and stored soils that calcium and magnesium ions not only do not increase but actually decrease in concentration.   On the other hand, from a similar comparison of pH values, there is an increase in alkalinity incidental to cropping in six out of seven cases. In view of the limited number of cases at hand and certain inconsistencies in the data as a whole, it is not clear that increased alkalinities are the only cause of decreased phosphate concentrations.

There are substantial increases in sulfate concentration in cropped and fallowed soils over and above those of stored soils, in all but one case.   We observe that the greatest increases are in the fallowed soils, although the cropped soils are not much lower.   It is not clear from the present data, whether the increase of this ion is due to oxidation of organic sulfur or to solution of solid-phase sulfate, or both.   The significant fact to be noted here is the relative quantitative importance of this ion.   In all of our soils which have been depleted in nitrate and chloride content, it is the most abundant ion.   The fact suggests itself that in non-alkaline soils, free from excess of chlorides, carbonates and bicarbonates, sulfate is the ion which is mainly responsible for keeping cations in solution when nitrates are diminished.   It seems to the writers that this, rather than the usefulness of sulfur as such to the plant, may be the cause of the greatly increased crops frequently obtained by sulfur applications to many soils.

SEASONAL CHANGES IN THE SOIL SOLUTION

In table 4 are presented the analyses of solutions displaced from the seven soils at the beginning and at the end of the ninth growing season, and at the beginning of the tenth season.   The data thus cover the critical periods for an

[4] See footnote 3.

entire year. The data from table 4 are recalculated to uniform moisture for each soil in table 5, and the latter is used as the basis for the following discussion.

In considering these data, it must be kept in mind that the soils had all borne crops of barley for 9 consecutive years, while under observation in this laboratory. Many of the soils also had been under intensive cultivation for

TABLE 4

Solutions displaced from cropped (A) soils at beginning and at the end of the growing season (1923) and at the beginning of the next growing season (1924)

SOIL NUMBER	DATE	MOISTURE	pH	PARTS PER MILLION OF DISPLACED SOLUTION							
				NO₃	HCO₃	SO₄	PO₄	Ca	Mg	Na	K
		per cent									
7	Apr. 30, 1923	10.7	7.4	174	83	655	1.1	283	106	49	24
	Sept. 4, 1923	12.5	7.6	58	155	432	0.6	193	47	40	9
	Apr. 28, 1924	14.2	7.6	222	142	571	0.6	296	67	52	11
8	Apr. 30, 1923	9.6	7.4	274	93	633	2.5	267	93	31	20
	Sept. 4, 1923	8.4	7.6	88	143	275	1.4	153	56	28	11
	Apr. 28, 1924	13.2	7.2	227	107	441	2.1	232	78	23	10
9	Apr. 30, 1923	11.4	7.6	160	73	432	0.9	213	75	27	12
	Sept. 4, 1923	13.8	7.8	43	167	121	0.3	107	32	30	7
	Apr. 28, 1924	12.9	7.6	182	98	390	0.5	220	57	28	10
10	Apr. 30, 1923	13.9	7.2	230	40	360	1.2	187	145	23	33
	Sept. 4, 1923	14.4	7.6	40	112	241	0.7	108	38	16	23
	Apr. 28, 1924	16.0	7.2	200	73	423	1.1	216	70	17	25
11	Apr. 30, 1923	12.9	8.2	166	160	645	3.3	213	93	84	39
	Sept. 4, 1923	12.4	7.6	16	234	598	1.2	192	64	44	22
	Apr. 28, 1924	11.4	8.1	286	259	854	2.9	300	102	85	38
12	Apr. 30, 1923	12.1	7.3	115	40	281	2.3	120	46	27	13
	Sept. 4, 1923	13.5	7.6	50	68	184	0.7	80	28	12	9
	Apr. 28, 1924	13.7	7.3	156	49	313	0.7	156	50	18	10
14	Apr. 30, 1923	18.0	8.0	146	107	295	1.3	140	47	56	45
	Sept. 4, 1923	18.7	7.6	13	176	174	0.2	80	23	26	23
	Apr. 28, 1924	18.8	7.6	167	142	380	1.0	168	55	47	49

years before they were assembled for experimental purposes. All soils have now reached a comparatively low yield which varies little from year to year. The average yield of grain in 1923 was about 39 per cent and total dry matter 29 per cent of that obtained in 1915. Under such circumstances, we might legitimately anticipate that whatever changes occur during a given growing season, the condition of the soil at the beginning of each season should be

relatively constant. Such a result is abundantly confirmed by the data presented. Briefly stated, these show that the resultant effect of a crop is to bring about a general diminution of concentration of electrolytes, especially of nitrates, sulfates, and bases in the solutions displaced from the soil, but that there is a tendency toward increased concentrations of such constituents after

TABLE 5

Solutions displaced from cropped (A) soils at the beginning and at the end of the growing season
(1923), and at the beginning of the next growing season (1924)

(Results from table 4 calculated to a uniform moisture basis for each soil)

SOIL NUM- BER	DATE	MOIS- TURE	pH	PARTS PER MILLION OF DISPLACED SOLUTION								
				NO₃	HCO₃*	SO₄	PO₄*	Ca	Mg	Na	K	Total
		per cent										
7	Apr. 30, 1923		7.4	149	83	561	1.1	242	91	42	21	1190
	Sept. 4, 1923	12.5	7.6	58	155	432	0.6	193	47	40	9	935
	Apr. 28, 1924		7.6	252	142	649	0.6	336	76	59	12	1527
8	Apr. 30, 1923		7.4	313	93	723	2.5	305	106	35	23	1601
	Sept. 4, 1923	8.4	7.6	88	143	275	1.4	153	56	28	11	755
	Apr. 28, 1924		7.2	357	107	693	2.1	365	123	36	16	1699
9	Apr. 30, 1923		7.6	132	73	357	0.9	176	62	22	10	833
	Sept. 4, 1923	13.8	7.8	43	167	121	0.3	107	32	30	7	507
	Apr. 28, 1924		7.6	170	98	365	0.5	206	53	26	9	928
10	Apr. 30, 1923		7.2	222	40	347	1.2	180	140	22	32	984
	Sept. 4, 1923	14.4	7.6	40	112	247	0.7	108	38	16	23	585
	Apr. 28, 1924		7.2	222	73	470	1.1	240	78	19	28	1131
11	Apr. 30, 1923		8.2	173	160	671	3.3	222	97	87	41	1454
	Sept. 4, 1923	12.4	7.6	16	234	598	1.2	192	64	44	22	1171
	Apr. 28, 1924		8.1	263	259	785	2.9	276	94	78	35	1793
12	Apr. 30, 1923		7.3	103	40	252	2.3	108	41	24	12	582
	Sept. 4, 1923	13.5	7.6	50	68	184	0.7	80	28	12	9	432
	Apr. 28, 1924		7.3	158	49	318	0.7	158	51	18	10	763
14	Apr. 30, 1923		8.0	141	107	284	1.3	135	45	54	43	810
	Sept. 4, 1923	18.7	7.6	13	176	174	0.2	80	23	26	23	515
	Apr. 28, 1924		7.6	168	142	382	1.0	169	55	47	49	1013

* Bicarbonate and phosphate remain as in table 4 (see text.)

the removal of the crop, and by the beginning of the succeeding season these are of the same general magnitude as those of the preceding year in soils which have been continuously cropped. In the light of these results, there can be but little doubt that the reason why a depleted soil continued to give fairly

uniform crops for many years is that it attains an equilibrium which is a function of environmental conditions and the nature of the solid phase. The comparatively small amounts of solutes removed from year to year by the growing plants do not substantially change the composition of the solid phase and hence cannot materially affect the equilibrium.

As stated above, most constituents decrease in concentration in the displaced solutions at the end of the growing season and apparently the losses of dissolved materials incidental to the growing of the crop have not at that time been made good by additions from the solid or gaseous phase. The exception to this generalization is the bicarbonate ion, which is invariably higher at the end than at the beginning of the growing season. The characteristic increase of the partial pressure of CO_2 in the soil atmosphere during the period of ripening of plants as shown by Russell and Appleyard (5) is sufficient to account for the increase of the bicarbonate ion at that stage.

The behavior of phosphate here, as in the cases already considered, is of interest. It seems clear that, whatever the cause, there is a general tendency for phosphate concentrations to diminish during the growing season and to increase during the period between crops. For the most part these fluctuations are consistent with the increases and decreases of alkalinity indicated by the pH values. Here again, however, certain exceptions[5] preclude definite conclusions and it is evident that more highly specialized experiments will be necessary to elucidate all of the vagaries of phosphate behavior.

From both sets of experiments, it seems fair to conclude that in soils which are not subject to the leaching effect of percolating waters, phosphate tends to be reduced in concentration when subjected to conditions incidental to the growing of a crop in spite of the tendency of solid-phase phosphates to dissolve and compensate for the amounts removed by the plant. The generally recognized tendency of many soils to increase in alkalinity during the growing season is probably the most important factor in the decrease of phosphate concentration found at that time. It should, however, be kept clearly in mind that the present data are derived from experiments in which soils were kept in tanks that permitted no escape of drainage water. It is, therefore, still an open question as to how the soil solutions of natural soils with good under-drainage are affected. Soils in which the effects of leaching are to reduce the concentration of calcium and magnesium should tend toward increased (3) concentrations of phosphate in the absence of increases in pH values. With concurrent decreases of alkalinity the effect should be accentuated. This phase of phosphate behavior is now undergoing study in this laboratory.

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[5] Inaccurate determinations of pH values may be the cause of these exceptions due to losses of CO_2 from the displaced solutions during the manipulation. It seems probable that very slight changes in the pH value cause substantial changes in phosphate concentration, so that experimental errors, unless quite small, become significant.

NATURE AND CHANGES OF THE SOIL SOLUTION

The uniformity in behavior with respect to most of the characteristics and changes observed in the displaced solutions from all of the soils studied renders it probable that many of the conclusions arrived at are applicable to soils in general.   Thus the evidence presented may be deemed to be conclusive that, excepting soils which are in a very high state of fertility, fallowing increases the concentration of the displaced solution and presumably also of the soil solution. On the other hand, the effect of cropping is to reduce the concentrations of most constituents in the displaced solution.   When soils have reached a low state of fertility due to continuous cropping the seasonal decrease of concentration to which most of the solutes are subject, is only temporary.   In such soils it may be expected that the initial concentration of the soil solution in any given growing season will be restored to its original magnitude by the beginning of the following season.

In addition to these broad generalizations the nature of the evidence would appear to justify a further statement of a quantitative character as to concentrations and changes of the soil solution in soils consisting largely of mineralized solid-phase constituents.   Soils approaching the extremes of mineralogical composition and those consisting largely of organic detritus are obviously beyond the scope of the present data.   Since we are in the nature of the case dependent upon observations of a limited number of specific individual soils we have first to consider the character of our particular soils with reference to their availability for such generalizations.

The investigations of Hilgard, and of his colleagues and successors, have clearly shown that soils of the arid region in general, not only contain larger totals of the bases used by plants than do the soils of humid regions, but also yield larger amounts of such bases when treated with various solvents.   The evidence afforded by water extractions is particularly cogent and gives indubitable proof of the relatively high degree of solubility of the constituents of typical arid soils.   Observations of freezing-point depressions also show substantially higher total concentrations for soils of arid, as compared with those of humid, regions.   The soils considered in the present paper are from a region of deficient rainfall and, while neither alkaline nor saline in the sense in which these terms are commonly used, are certainly typical of their climatic origin.   As such, the total concentrations of their soil solutions are probably higher than those of the average soil from humid regions.   The absolute concentrations of electrolytes in the soil solution inferred from studies of the solutions displaced from our soils, thus probably represent maxima which are not likely to be attained in humid soils, save in exceptional cases.   With this understanding we may venture to suggest certain characteristics of the conventional soil solution based upon the present data.   Referring to table 3, the highest total concentration we have yet observed in a displaced solution was in the stored soil 8, which contained 4093 parts per million at 14.7 per cent moisture.   If

such a soil were reduced to half this moisture content, as might easily happen under cultural conditions in the field, the concentration should approximately double.   It seems fair to conclude that the soil solution of soils in general probably seldom exceeds 5000 parts per million at moisture contents corresponding to their optimal water requirements, or 10,000 parts per million at half optimum.

When the concentration of the soil solution is of this order of magnitude it is probably not greatly increased by fallowing and may be diminished thereby. When of lower concentration, and in the generality of cases, the concentration is probably increased by any treatment which stimulates biological activities. With soils having solutions of very low concentrations such treatment may greatly increase the amounts of dissolved matter (cf. 12 S and 12 B).   On the other hand, there is but little doubt that cropping a soil continuously even for a limited number of years decreases the concentration of the soil solution in all soils and the greatest rate of loss is probably in those soils which initially had high concentrations (cf. 8S with 8A and 12S with 12A).   Soils probably will not prove highly productive when the soil solution at the beginning of the growing season approaches a concentration of 1000 parts per million at optimum moisture content, unless the rate of formation of solutes and particularly of nitrates is especially high during the period covering the early stages of the growth of the crop.

When a soil has been continuously cropped for a number of years it probably seldom contains more than 1500 parts per million of total solutes in its soil solution, and the quantity may be considerably lower than 1000 parts per million at optimum moisture even at the beginning of the growing season.   Such soil solutions decrease still further during the growth of the crop and may be reduced to a few hundred parts per million by the end of the period of absorption by the plant, after which they tend to increase and may return to their initial concentrations by the beginning of the next season.

The qualitative characteristics of the soil solution may be made clearer by expressing the results in terms of chemical equivalents.   For this purpose we have averaged the data (see table 3) from each set of soils and recomputed these in terms of milli-equivalents.   These results are presented in table 6A.   It will be observed that the sums of the negative ions are somewhat less than those of the positive ions.   The differences are given in the column headed "deficiency."   These differences are doubtless due to analytical errors inseparable from determinations based on small quantities of solution.   In table 6B we have eliminated the deficiency by proportionate additions to all negative ions.

From table 6B it is evident that the solutions from stored and fallowed soils have the same general qualitative characteristics, consisting largely of nitrates and sulfates, the ratio of nitrate to sulfate being about 3 to 1 in both sets of soils.   In the depleted soils this is reversed and the nitrate-sulfate ratio is about 1 to 3.   A further change occurs during the growth of crops as shown by the individual soils in table 5 where the nitrate decreases, bicarbonate increases

and sulfate, while usually decreasing, does not ordinarily diminish at so great a rate as does nitrate.   The effect upon the proportions of the various anions, however, is minimized here because all of the soils had comparatively low amounts of nitrates at the beginning of the season due to the continuous cropping to which they had been subjected.   It is evident that highly fertile soils comparable to most of the "B" or "S" soils, would suffer an extreme reversal of anion composition during the growth of a crop, since the previous work of this laboratory (1) has shown that even such soils lose the greater part of their nitrates after the first few weeks of the growth of barley.   The data from the

TABLE 6 A

Average composition of displaced solutions from cropped (A), fallowed (B) and stored (S) soils
after 8 years*

SOILS	MOIS- TURE	NEGATIVE IONS MILLI-EQUIVALENTS							POSITIVE IONS MILLI-EQUIVALENTS				TOTAL IONS MILLI- EQUIVA- LENTS
		NO₂	HCO₃	Cl	SO₄	PO₄	SiO₃	Defi- ciency	Ca	Mg	Na	K	
	per cent												
A	12.6	2.91	1.44	0.0	9.81	0.06	1.26	4.29	10.14	7.10	1.84	0.68	39.54
B	16.3	25.12	0.87	1.22	8.21	0.06	1.26	6.50	27.88	10.99	2.77	1.61	86.49
S	16.2	16.80	1.20	7.41	4.96	0.17	1.26	2.98	19.02	8.80	5.04	1.92	69.56

* Averages from table 1.

TABLE 6 B

Average composition of displaced solutions from cropped (A), fallowed (B) and stored (S) soils
after 8 years after eliminating deficiency*

SOILS	MOISTURE	NEGATIVE IONS MILLI-EQUIVALENTS						POSITIVE IONS MILLI-EQUIVALENTS				TOTAL IONS MILLI- EQUIVA- LENTS
		NO₃	HCO₃	Cl	SO₄	PO₄	SiO₃	Ca	Mg	Na	K	
	per cent											
A	12.6	3.72	1.84	0.00	12.53	0.08	1.61	10.14	7.10	1.84	0.68	39.54
B	16.3	29.56	1.02	1.44	9.66	0.07	1.48	27.88	10.99	2.77	1.61	86.49
S	16.2	18.37	1.31	8.10	5.43	0.19	1.38	19.02	8.80	5.04	1.92	69.56

* Averages from table 1.

"A" and "S" soils (table 6B) are therefore probably more representative of the qualitative changes in ordinarily fertile soils during the growing season than are those from the seasonal study of the depleted soils.   The special interest of the qualitative changes in the soil solution of soils under crop, lies in the fact that the make-up of many nutrient culture solutions has been based upon the imagined composition of the conventional soil solution.   We may, therefore, consider what the composition of such a nutrient culture solution should be if it is to simulate the concentration of the soil solution as it exists at any given period.   For this purpose we have re-calculated the data from

table 6B in terms of parts per million of the salts which would supply the amounts of solutes shown by the averages of our displaced solutions. These data are presented in table 7.

The combinations of ions, of course, are purely conventional and are based upon the relative solubilities of the various salts. It is not intended to imply that the ions as they exist in the displaced solutions are in these particular combinations or are undissociated. Such a tabulation, however, brings out the extraordinary qualitative differences of composition which must be taken into account when the liquid phase of soils under crop is being considered. Moreover, the results indicate in a more definite manner than we have been able to present heretofore, that a nutrient solution made up in imitation of

TABLE 7

Conventional combinations as salts of ions in displaced solutions from cropped, fallowed and stored soils after 8 years

SALT	CROPPED (12.6 PER CENT WATER)		FALLOWED (16.3 PER CENT WATER)		STORED (16.2 PER CENT WATER)	
	p.p.m.	Proportion	p.p.m.	Proportion	p.p.m.	Proportion
		per cent		*per cent*		*per cent*
NaNO$_3$.................	156	11.40	235	7.15	428	17.04
KNO$_3$.................	69	5.04	163	4.96	194	7.72
Mg(NO$_3$)$_2$..............	89	6.51	813	24.72	651	25.92
Ca(NO$_3$)$_2$.............	—	—	1164	35.39	214	8.52
CaCl$_2$.................	—	—	80	2.43	450	17.91
MgSO$_4$.................	354	25.88	—	—	—	—
CaSO$_4$.................	451	32.97	657	19.98	369	14.69
Ca(HCO$_3$)$_2$..............	149	10.90	83	2.52	106	4.22
Ca$_3$(PO$_4$)$_2$..............	8	0.58	7	0.21	20	0.80
CaSiO$_3$.................	92	6.73	87	2.65	80	3.18
Total.................	1368	100.00	3289	100.00	2512	100.00
Total Computed to Uniform Water 16.2 per cent	1064		3309		2512	

the probable composition of the soil solution of fertile soils at the beginning of the season is anything but representative of the liquid phase of the soil as it exists at later periods if plants are being grown thereon.

SUMMARY

1. Data are presented covering the composition of the solutions displaced from seven fine sandy loam soils under varied conditions.

2. The conditions represented were those incidental to cropping, fallowing, and maintenance in the air-dry state, all for a period of 8 years.

3. Similar data obtained from the cropped soils at the beginning and at the end of the ninth season and at the beginning of the tenth season of continuous cropping are given.

4. It is concluded that continuous cropping invariably decreases the concentrations of the solutions obtainable from soils by water displacement. On the other hand, fallowing increases the concentrations of such solutions except in the case of soils in a high state of fertility.

5. In soils which have been continuously cropped for some years, the seasonal decrease of concentration of the displaced solution characteristic of soils in general is temporary, and it may be expected that such solutions will increase to their initial concentrations by the beginning of the next season.

6. The characteristic fluctuations in concentration of certain solutes in the displaced solution are discussed. The fluctuations of phosphate concentration are deemed to depend primarily upon the reaction of the soil solution, although the concentrations of certain cations also are involved.

7. Estimates of the quantitative composition of the soil solution of fertile and infertile soils are tentatively suggested.

8. Evidence is presented which tends to show that the qualitative composition of the soil solution in soils under crop is constantly changing. It follows that nutrient culture solutions made up in imitation of the soil solution as it exists at the beginning of the season, cannot represent such solution during the later stages of the growth of crops.

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